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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

ANTI-CANCER PEPTIDIES

N. E. Golubeva, O. V. Kil'disheva and Academician I. L. Knuniants

The condensation of the N-formyl derivative of p-di(β-chloroethyl)amino-DL-phenylalanine (sarcolysine) with esters of various amino acids gave anti-cancer dipeptides containing sarcolysin (Table 1).

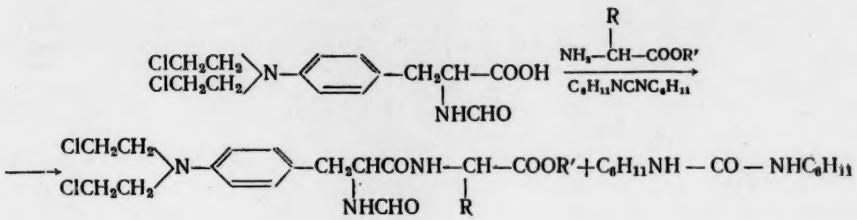
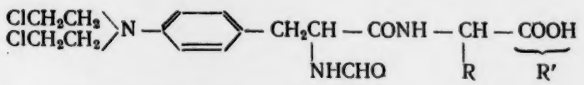
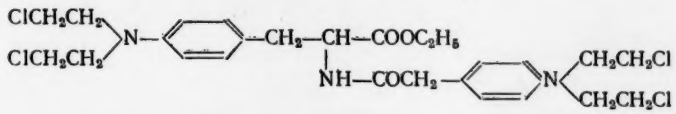


TABLE 1



№№	R		Found, %				Calculated, %				M.p., °C	Yield %	Recrystallized
			C	H	Cl	N	C	H	Cl	N			
1	$-CH_2-SCH_2CH_2Cl$	$-COOC_2H_5$	48.02	5.90		7.93	47.84	5.66		7.96	121—123	40	From ethanol
2	$-CH_2CH_2SCH_3$	$-COOC_2H_5$	51.27	6.45	14.46	8.73	51.22	6.35	14.40	8.54	109—110	70	From ethyl acetate
3	$-CH_2CH_2-$ $-SCH_2C_6H_5$	$-COOC_2H_5$	57.03	6.15	12.29	7.30	57.03	6.21	12.47	7.39	95—96	Quant	From petroleum ether
4	H	$-COOC_2H_5$	50.58	5.77	17.33	10.58	50.5	5.73	17.54	10.4	118—120	"	From ethanol

The reaction of the ethyl ester of sarcolysine with p-di(β-chloroethyl)aminophenylacetic acid gave the ethyl ester of p-di(β-chloroethyl)aminophenylacetylsarcolysine.



In addition, the p-di(β-chloroethyl)aminophenylacetyl and γ-[p-di(β-chloroethyl)amino] phenylbutyryl derivatives of various amino acids were prepared; the derivatives had the general formula:

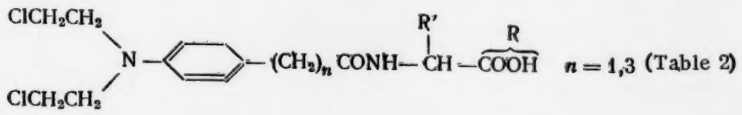
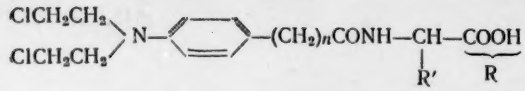


TABLE 2



n	R	R′	Found, %				Calculated, %				M.p., °C	Yield, %	Recrystallized
			C	H	Cl	N	C	H	Cl	N			
1	$-COOC_2H_5$	$-CH_2C_6H_5$	61.25	6.19	15.60	6.37	61.19	6.25	15.71	6.21	86—87	Quant.	From ethanol
1	$-COOC_2H_5$	$-CH_2CH(CH_3)_2$	57.42	7.27	16.37	6.9	57.54	7.24	16.98	6.71	81—82	47	From ethanol
1	$-COOCH_3$	H	51.87	5.97	20.4	—	51.88	5.81	20.42	—	85—86	68	From methanol
1	$-COOCH_3$	$-CH_2Cl$	48.71	5.58	27.20	—	48.60	5.32	26.92	—	113—114	79	From methanol
1	$-CH_2COOC_2H_5$	$-C_6H_5$	61.32	6.27	15.68	6.44	61.19	6.25	15.71	6.21	84—86	81	From ethanol
1	$-COOC_2H_5$	$-CH_2CH_2-S-CH_3$	52.18	6.39	15.90	6.37	52.41	6.48	16.29	6.44	46—49	91	From ethanol
1	$-COOC_2H_5$	$-CH_2CH_2SCH_2C_6H_5$	58.91	6.27	13.59	—	58.87	6.31	13.86	—	73—74	65	From ethanol
1	$-COOC_2H_5$	$-CH(CH_3)_2$	56.60	7.06	17.88	7.44	56.56	6.99	17.58	6.94	61—62	50	From ethyl acetate-petroleum ether
1	$-COOC_2H_5$	$-CH_2-S-CH_2CH_2Cl$	49.09	5.76	—	6.13	48.60	5.96	—	5.96	77—79	72	From ethanol
3	$-COOC_2H_5$	$-CH_2C_6H_5$	62.68	6.89	15.26	5.70	62.65	6.68	14.79	5.85	69—71	78	From ethanol
3	$-COOC_2H_5$	$-CH-(CH_3)_2$	58.47	7.70	15.75	6.37	58.46	7.48	16.44	6.5	62—63	92	From ethanol
3	$-CH_2COOC_2H_5$	$-C_6H_5$	62.53	6.73	14.75	—	62.65	6.68	14.79	—	84—86	Quant.	From ethanol
3	$-COOCH_3$	H	54.31	6.45	19.09	—	54.40	6.40	18.92	—	84—85	•	From methanol

The interaction of p-di(β-chloroethyl)aminophenylacetic and γ-[p-di(β-chloroethyl)amino]phenylbutyric acid with aniline in the presence of 1,3-cyclohexylcarbodiimide gave the corresponding anilides; however, when these acids were reacted with 2-methyl-5-ethoxymethylene-6-aminopyrimidine or when p-di(β-chloroethyl)aminophenylacetic acid was reacted with cyclohexyl amine, only N-acyl derivatives of 1,3-dicyclohexylurea were obtained.

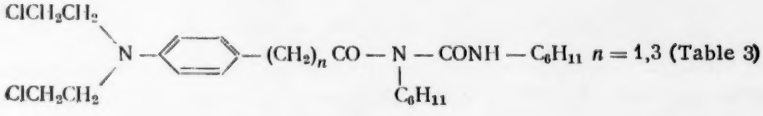


TABLE 3

n	R	Found, %				Calculated, %				M.p., °C	Yield, %	Recrystallized
		C	H	Cl	N	C	H	Cl	N			
1	$-NH-C_6H_5$	61.17	5.57	—	8.27	61.54	5.74	—	7.98	128—129	83	From octane
3	$-NH-C_6H_5$	62.89	6.31	18.50	6.92	63.32	6.38	18.7	7.39	112—113	Quant.	From octane
1	$-N(C_6H_{11})-CONH-C_6H_{11}$	61.68	7.60	15.00	—	62.21	7.73	14.69	—	130—131	89	From ethanol
3	$-N(C_6H_{11})-CONH-C_6H_{11}$	63.36	8.08	13.42	8.16	63.51	8.09	13.89	8.23	128	51	From ethanol

Preliminary testing of the anti-cancer action of peptides containing sarcolysine was carried out in the Institute of Experimental Pathology and Cancer Therapy of the Academy of Sciences, USSR. It was shown that sarcolysine peptides possess anti-tumor activity close to that of sarcolysine and, at the same time, are nontoxic and have a highly selective action on certain tumors [1].

General Method for the Preparation of Peptides Containing Sarcolysine

To a suspension of 1 mole of N-formylsarcolysine in chloroform equimolar amounts of 1,3-dicyclohexylcarbodiimide and the desired amino acid ester were successively added. The mixture was vigorously agitated and allowed to stand at room temperature overnight. The precipitated 1,3-dicyclohexylurea was filtered, and

the residue (after distillation of the chloroform) was mixed with a small amount of alcohol• and stored in a refrigerator for crystallization. The precipitated dipeptide was filtered (see Table 1).

Ethyl Ester of p-di(β-Chloroethyl)aminophenylacetylsarcolysine

Equimolar amounts of the ethyl ester of sarcolysine, p-di(β-chloroethyl)aminophenylacetic acid, and 1,3-dicyclohexylcarbodiimide were dissolved in chloroform and allowed to stand overnight. The precipitated 1,3-dicyclohexylurea was filtered, the solvent was distilled under vacuum, the residue was dissolved in ethyl acetate, petroleum ether was added until the solution became turbid, and the mixture was placed in a refrigerator to crystallize.

The ethyl ester of p-di(β-chloroethyl)aminophenylacetylsarcolysine had the form of colorless crystals with m. p. 92-94° (from ethanol). The yield was 95%.

Found %: C 54.81; H 5.93; Cl 24.09. $C_{27}H_{35}Cl_4N_3O_3$. Calculated %: C 54.82; H 5.92; Cl 24.03.

General Method for the Preparation of Esters of N-p-di(β-Chloroethyl)aminophenylacetyl- and N-γ-[p-di(β-Chloroethyl) amino]phenylbutyrylamino Acids

A mixture of equimolar amounts of p-di(β-chloroethyl)aminophenylacetic (or γ-[p-di(β-chloroethyl) amino] phenylbutyric) acid, ester of an amino acid,•• and 1,3-dicyclohexylcarbodiimide in chloroform was allowed to stand at room temperature overnight. The precipitated 1,3-dicyclohexylurea was filtered, the solvent was distilled, the residue was mixed with a small amount of alcohol,••• and the mixture was placed in a refrigerator to crystallize (see Table 2).

Anilides of p-di(β-Chloroethyl)aminophenylacetic and γ-[p-di(β-Chloroethyl) aminophenylbutyric acids

A mixture of equimolar amounts of aniline, the acids indicated above, and 1,3-dicyclohexylcarbodiimide was allowed to stand in chloroform overnight. The precipitated 1,3-dicyclohexylurea was filtered and carefully washed with chloroform. The solvent was distilled under vacuum. The resulting anilides were recrystallized from alcohol (see Table 3).

Ethyl Ester of s-β-Chloroethylcysteine

3 g of the hydrochloride of chloroethylcysteine was refluxed with 50 ml of C_2H_5OH saturated with HCl for 2 hours, during which a stream of dry HCl was passed through the mixture. The solvent was distilled to dryness. The hydrochloride of the ethyl ester of chlorocysteine had the form of colorless needles with m. p. 108-110°. The yield was 81%.

Found %: C 33.83; H 6.01. $C_7H_{15}Cl_2NO_2S$. Calculated %: C 33.83; H 6.09.

N-p-di(β-Chloroethyl)aminophenylacetyl and N-γ-[p-di(β-Chloroethyl)amino] phenylbutyryldicyclohexyl urea

A mixture of equimolar amounts of p-di(β-chloroethyl)aminophenylacetic or γ-[p-di(β-chloroethyl) aminophenylbutyric acid, 1,3-dicyclohexylcarbodiimide, and 2-methyl-5-ethoxymethylene-6-aminopyrimidine

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• In the preparation of the ethyl ester of N-formylsarcolysylmethione, the residue was dissolved in ethyl acetate, and petroleum ether was added until the solution became turbid.

•• The ethyl ester of s-β-chloroethylcysteine was used in the form of an oil; it was separated form its hydrochloride with sodium bicarbonate.

••• In the case of the condensation of γ-[p-di(β-chloroethyl)-amino]phenylbutyric acid with the esters of phenylalanine and valine, the residue was dissolved in ethyl acetate, and petroleum ether was added until the solution became turbid.

was dissolved in chloroform and allowed to stand overnight. The solvent was distilled, and the residue was mixed with ethyl alcohol and left to crystallize (see Table 3).

Institute of Heteroorganic Compounds
Academy of Sciences USSR

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*Original Russian pagination. See C.B. Translation.

X-RAY INVESTIGATION OF 1,4-DIANILINOANTHRAQUINONE AND 1,4-DIMESIDINOANTHRAQUINONE

N. S. Dokunikhin, G. A. Gol'der and G. S. Zhdanov

(Presented by Academician N. V. Belov, November 20, 1957)

The sulfonic acids of 1,4-di(arylamino)anthraquinone comprise an important group of fast dyes for wool. A large part of the 1,4-di(arylamino)-substituted anthraquinones are green; derivatives in which the substituents are all ortho to hydrogen atoms of the aryl groups constitute an exception. Such compounds, and also the corresponding alkylamino and hydroarylamino derivatives, have an intense, bright blue color.

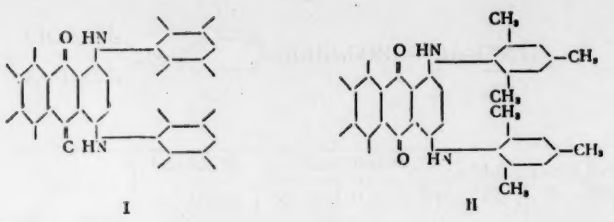
The change in the absorption of light by CCl_4 solutions of 1,4-di(arylamino) anthraquinones in the visible and ultraviolet regions of the spectrum shows that when methyl or ethyl groups or bromine atoms are present in all ortho positions of the phenyl radicals or in the 2,3-positions of the anthraquinone, there is no absorption in the short-wave region of the spectrum, and the main maximum shifts in the direction of shorter wave lengths [1]. Inasmuch as the enumerated groups are known to exclude disposition of the phenyl radicals in the plane of the basic part of the molecule, an appearance of additional absorption bands and a deepening of the main band must, in the absence of steric hindrance, be recognized as a consequence of coplanarity of the molecule. A comparison of absorption frequencies in the infrared region of the spectrum [2] also supports this proposition.

	λ (N–H), cm^{-1}	λ (C–O), cm^{-1}
1,4-di(p-tolylamino)anthraquinone	3120	1620
1,4-di(mesitylamino) anthraquinone	3175	1630
1,4-di(p-tolylamino)-2,3-dimesitylanthraquinone	3230	1640

These data indicate a weakening of the intramolecular hydrogen bond formed by the carbonyl oxygen with a hydrogen of the amino group when a co-planar disposition of the benzene rings is sterically hindered. This weakening of the hydrogen bond is a result of an increase in bond length caused by the emergence of the hydrogen from the plane of the anthraquinone rings, and may be explained by a disturbance of the conjugated system [3].

For these compounds, π-electron interaction of the nitrogen atoms with the aromatic rings to which they are attached must be recognized as a force for holding the phenyl radicals in the plane [4, 5]. Since the presence of such interaction is of considerable value in understanding the chemistry and color, not only of a large number of commercially important arylamino derivatives of anthraquinone, but also of many other secondary aromatic amines, it was desirable to obtain direct proof of the planar structure of molecules of derivatives of 1,4-di(arylamino)anthraquinone in which steric hindrance is absent.

In order to answer the question of the co-planarity of the benzene rings with the plane of the basic part of the molecule, x-ray measurements of crystals of two compounds were carried out:



I II

1,4-dianilinoanthraquinone (I) and 1,4-dimesidinoanthraquinone (II).

In a free molecule of compound I, steric hindrance is possible between the CH groups of the anthraquinone and benzene rings, which forces deflection of the latter through an angle of ~20° relative to the plane of the basic part of the molecule (if the C–N–C angle is assumed to be a right angle). In a free molecule of compound II, the presence of CH_3 groups joined to the benzene ring forces it to turn through an angle of not less than 60° relative to the plane of the anthraquinone nucleus.

TABLE 1

Compound	Unit cell dimensions				Density		No. of molecules	Space group
	a, A	b, A	c, A	β	pycnom.	x-ray		
1,4-Dianilinoanthraquinone (I)	12.2	8.73	17.8	108°	1.51	1.52	4	$C_{2h}^5 - P2_1/c$
1,4-Dimesidinoanthraquinone (II)	7.98	19.8	17.2	103°	1.20	1.28	4	$C_{2h}^5 - P2_1/c$

In Table 1 are presented the results of x-ray measurements of the unit cells, the space groups, and the densities of the compounds indicated above. On the basis of a consideration of the dimensions of the unit cell

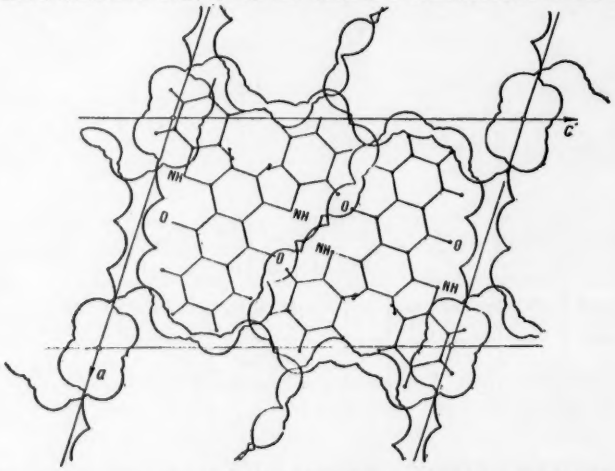


Fig. 1. Arrangement of the 1,4-dianilinoanthraquinone molecules in projection on the ac plane (only one layer of molecules shown)

of compound I, it can be assumed that the basic part of the molecule of this compound is parallel or almost parallel to the ac plane, since the b axis is the shortest (8.73 A). From the symmetry conditions of space group $C_{2h}^5 = P2_1/c$, it follows that there is a glide-plane perpendicular to the b axis with a shift along the c axis, as a consequence of which, with 4 molecules present in the unit cell, the molecules are arranged in layers perpendicular to the b axis. A variant of such an arrangement is shown in Figure 1. This arrangement permits an insignificant rotation of the benzene ring relative to the remainder of the molecule and also a certain possible rotation of the entire molecule relative to the ac plane. Consequently, packing of the molecules in the crystal does not require an additional change in the angle of rotation of the benzene ring in comparison with the free molecule.

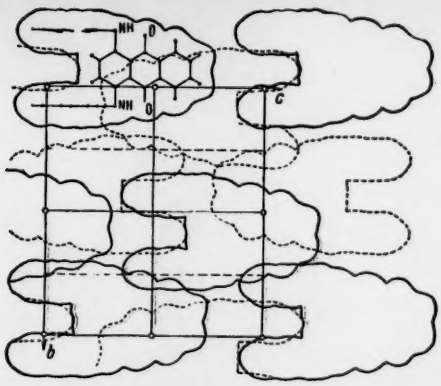


Fig. 2. Arrangement of molecules of 1,4-dimesidinoanthraquinone in projection on the bc plane. Continuous lines show molecules of a single layer; the broken lines represent another layer (not all molecules in the unit cell are shown).

The shortest axis in a crystal of compound II is the a axis (7.98 A). Its length almost coincides with the dimensions of the benzene ring and the CH_3 group joined to it (8.8 A). Dense packing of the molecules in the crystal and fulfillment of the symmetry conditions for the space group to which molecules of compound II belong can be realized with the arrangement of molecules shown in Figure 2. As seen from the figure, in this variant, the benzene rings are turned in an angle equal or close to 90° relative to the main part of the molecule.

The benzene rings of neighboring molecules are as though meshed with each other, thereby causing dense packing. An arrangement of the molecules in which the benzene rings are not meshed would not permit the unit cell dimensions found. As a consequence of this arrangement of the molecules in the crystals of compound II, the possibility of twisting vibrations of the associated benzene rings is practically excluded.

In the absence of steric hindrance, as is the case in a molecule of, for example, 1,4-dianilinoanthraquinone, the associated benzene rings remain almost co-planar with the main part of the molecule, as is shown by the x-ray investigation of crystals of this compound. In this case, as proposed above, π-electron interaction of the nitrogen atoms with the aromatic rings retains its essential significance.

The addition of methyl groups in all meta positions of the benzene ring creates such a considerable steric hindrance in the molecules that, as shown by the x-ray investigations of crystals of 1,4-dimesidinoanthraquinone, the deviation from co-planarity with the anthraquinone nuclei is close to 90°. As shown by spectroscopic data, a consequence of this is considerable weakening of the intramolecular bonds.

K. E. Voroshilov Scientific
Research Institute of
Intermediate Products and Dyes
L. Ia. Karpov Physicochemical
Scientific Research Institute

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•Original Russian pagination. See C.B. Translation.

CERTAIN FEATURES OF CARBONIUM-ION POLYMERIZATION OF THE SYSTEM STYRENE-α-METHYLSTYRENE

E. B. Liudvig, A. R. Gantmakher and
Corresponding Member AN SSSR S. S. Medvedev

The present work was devoted to an investigation of the cationic copolymerization of styrene with α-methylstyrene. This system was first studied by us, and we discovered the phenomenon of a sharp increase in the rate of polymerization of styrene in the presence of small amounts of α-methylstyrene.

The dependence of the rate of copolymerization on the composition of the initial mixture was investigated, and the compositions and molecular weights of the corresponding polymers were determined. These data were compared with results obtained during an investigation of the polymerization of the individual monomers.

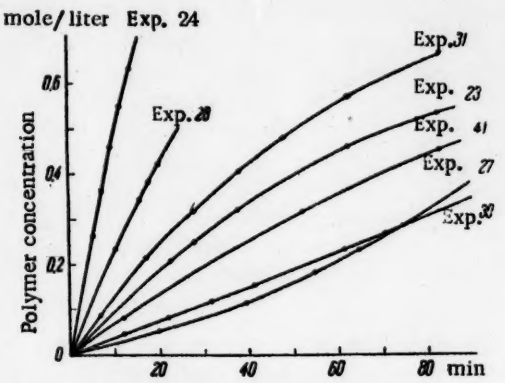

Fig. 1. Copolymerization rate of the system styrene-α-methylstyrene. $SnCl_4$ concentration 0.002 mole/liter. Total monomer concentration 2.5moles/liter. Initial ratio of styrene to α-methylstyrene (mole): Exp. 24–0:1; Exp. 28–1:4; Exp. 31–1:2.5; Exp. 23–1:1; Exp. 30–2.5:1; Exp. 27–4:1; Exp. 41–1:0.

Particular attention was paid to the investigation of the kinetics in the presence of low concentrations of the more active monomer —α-methylstyrene. The effects of the following factors on the acceleration observed in this concentration region were studied: temperature, catalyst concentration, total monomer concentration, and the addition of water and of hydrogen chloride. The polymerization was carried out at 0° with a catalyst consisting of an ethyl chloride solution of $SnCl_4$. The rate was determined dilatometrically. The compositions of the copolymers were determined by infrared spectroscopy. The method used was a comparison of the spectra of the copolymers with those of mixtures of the individual polymers. The molecular weights of the copolymers were determined by osmosis.

The kinetic curves obtained for various initial ratios of monomers (see Figure 1) show that in the range of α-methylstyrene concentration of from 0.7 to 1.7 moles/liter (with a total monomer concentration of 2.5 moles/liter), copolymerization of styrene with α-methylstyrene proceeds without an induction period and with a gradually decreasing rate.

A comparison of the compositions of the copolymers with the compositions of the initial mixtures is given in Table 1; it follows from these data that the copolymers are very strongly enriched with α-methylstyrene, the more active component.

On the basis of the data on the compositions of the copolymers, the copolymerization constants were determined with the aid of the composition integral: $\alpha = 0.05$ (styrene); $\beta = 2.90$ (α-methylstyrene). As seen

from these data, the product of the copolymerization constants for this system is less than unity; this is due to the action of polar or steric factors [1, 2]. In cationic polymerization, any tendency toward alternation of the monomers is due solely to the action of the steric factor. In the present system, the rate of the reaction of the α-methylstyrene carbonium ion with its own monomer is decreased by the presence of two substituents on one of the doubly bonded carbon atoms.

TABLE 1

Expt. No.	Initial styrene to α-methyl-styrene (mole)	Styrene-to-α-methyl-styrene ratio (mole) in copolymers	Depth of polymerization, %
89	21.5 : 1	5.3 : 1	5.9
16	10.8 : 1	1.77 : 1	2.3
14	4.3 : 1	0.75 : 1	12.9
10	1.1 : 1	0.30 : 1	20.3
1	0.75 : 1	0.20 : 1	9.2
17	0.47 : 1	0.13 : 1	27.3

TABLE 2

Expt. No.	Initial styrene to α-methyl-styrene	Molecular weight	Depth of polymerization, %
94	1 : 0	70.000	
67	22.5 : 1	54.900	58.6
63	11.3 : 1	47.000	73.0
89	21.5 : 1	28.200	5.9
27	4.5 : 1	23.800	24.7
23	1.14 : 1	26.400	22.0
31	0.47 : 1	21.400	27.4
28	0.28 : 1	23.500	19.0
54	0 : 1	26.700	50.2

The steric effect also appears during the polymerization of α-methylstyrene alone; this is confirmed by the heat of polymerization [3].

The molecular weights of the polymers are presented in Table 2.

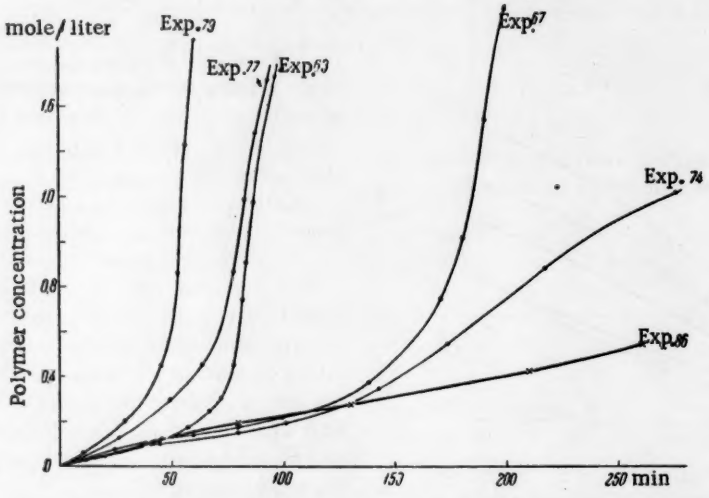

Fig. 2. Copolymerization rates in the system styrene-α-methylstyrene at low α-methylstyrene concentrations. $SnCl_4$ concentration 0.002 mole/liter. Total monomer concentration 2.5 moles/liter. Initial ratio of styrene to α-methylstyrene (mole): Exp. 74—4:1; Exp. 67—21:1; Exp. 63—13:1; Exp. 79—20:1 (at triple $SnCl_4$ concentration of 0.006 mole/liter); Exp. 77—50:1 (at triple $SnCl_4$ concentration); Exp. 86—20:1 (total monomer concentration increased by a factor of 1.6).

The kinetics in the region of low concentrations of the more active component are of the greatest interest. The kinetic curves for this region are shown in Figure 2. A characteristic of these curves is the considerable increase in polymerization rate with time, this increase beginning at a specific stage in the polymerization characteristic for each of the given monomer ratios. The depth of polymerization at the beginning of this acceleration and the value of the maximum rate depend on the initial monomer ratio. The high-

est maximum rate was observed for a ratio of 10 moles of styrene to 1 mole of α-methylstyrene.* It was shown that the polymerization rate increased and the depth of polymerization corresponding to the initiation of the acceleration decreased with an increase in the catalyst concentration and also with an increase in total monomer concentration (Figure 2). In addition, the time to the initiation of acceleration was inversely proportional to the concentrations of catalyst and α-methylstyrene, and did not depend on the styrene concentration; the maximum rate was proportional to the α-methylstyrene concentration and to the square of the styrene concentration.

The temperature had a considerable influence on the observed effect; a decrease in temperature considerably decreased the ratio of the maximum to the initial rate and increased the induction period.

The observed maximum rates considerably exceeded the sum of the polymerization rates for the individual monomers at the same initial concentrations.

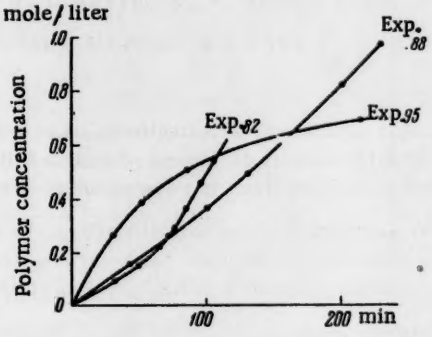

Fig. 3. Effect of the addition of water and of HCl on the copolymerization rate in the system styrene-α-methylstyrene at low α-methylstyrene concentrations. $SnCl_4$ concentration 0.002 mole/liter. Total monomer concentration 2.5 moles/liter. Initial ratio of styrene to α-methylstyrene (mole): Exp. 82–10:1; ([HCl] = 0.004 mole/liter); Exp. 88–10:1 ([HCl] = 0.010 mole/liter); Exp. 95–20:1 ([$SnCl_4$] = 0.006 mole/liter, [H_2O] = 0.012 mole/liter).

As seen from Table 2, the average degree of polymerization of the polymers obtained when acceleration occurred (Experiments Nos. 63 and 67) was lower than the degree of polymerization of polystyrene (Experiment No. 94) obtained under the same conditions. In addition, the maximum rate when acceleration was present was 26 times (at a mole ratio of styrene to α-methylstyrene of 10:1) and 14 times (at a mole ratio of 20:1) the polymerization rate of styrene.

It follows from these data that the observed increase in rate is connected with initiation reactions.

In support of this proposition is the sharp effect on the acceleration of the addition of water and hydrogen chloride. A seen from Figure 3, the acceleration was strongly retarded by the addition of water and HCl. Below, we dwell on possible reasons for the small increase in rate in the presence of high concentrations of HCl.

It is well known that molecules of water and HCl readily form complexes with Friedel-Crafts catalysts. Tying up the catalyst in a complex, they thereby must change the initiation conditions, and, consequently, they effect all of the processes connected with initiation. Therefore, their effect on the increase in rate with time in a given case is in agreement with the proposal that this increase is dependent on initiation reactions. Apparently, in this system there is a selective complex formation of α-methylstyrene with $SnCl_4$, which causes a high initiation rate in the presence of small amounts of this monomer. From the observed dependence of

* In experiments with a very high acceleration, the polymerization process proceeded nonisothermally. However, owing to the small temperature coefficient of this process, the observed temperature increase had little effect on the reaction rate.

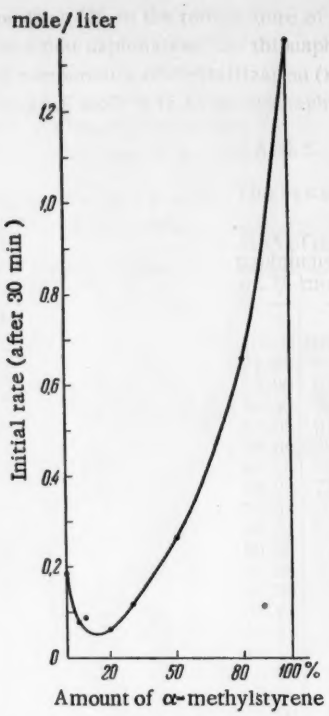

Fig. 4. Dependence of initial copolymerization rate in the system styrene-α-methylstyrene on initial component ratio. $SnCl_4$ concentration 0.002 mole/liter. Total monomer concentration 2.5 moles/liter.

the rate on concentration of the components, it follows that the formation of the initial active center proceeds by means of a reaction of the catalyst-α-methylstyrene complex with the styrene. Concurrent complex formation of the $SnCl_4$ with HCl or H_2O must decrease the rate increase, as was observed experimentally.

Another interesting fact observed in the region of low initial α-methylstyrene concentrations was the partial reduction of the initial rate of polymerization of styrene with the introduction of small amounts of α-methylstyrene (Figure 4).

The inhibition of the polymerization of the less active monomer by small amounts of the more active monomer is well known in radical polymerization. It is due to the antagonism between the activity of the monomer and that of the corresponding radical. In ionic polymerization, owing to the absence of a method for the determination of individual chain-propagation constants, such antagonism cannot be established by direct methods.

The observed decrease in the initial rate of polymerization of styrene caused by small amounts of α-methylstyrene is an indirect indication that such antagonism occurs here also.

Owing to the depletion of α-methylstyrene as the process proceeds, the polymerization rate must increase somewhat, approaching the polymerization rate for pure styrene.

The effect of the addition of H_2O and HCl on decreasing the acceleration, which is apparently dependent on initiation reactions, makes it possible to detect the acceleration of the process due to an increase in chain-progagation rate with the depletion of the low-activity α-methylstyrene carbonium ions (see curve for Exp. 82 in Figure 3, and also Table 2, Experiments Nos. 89 and 67).

Thus, in the present work it was shown that the reactivity of a molecule of α-methylstyrene with respect to a styrene carbonium ion is considerably higher than the reactivity of styrene, and that the addition of this more active component causes a sharp increase in the rate of styrene polymerization. The observed effect has, apparently, a more general character and is connected with a sharp difference in monomer activities, since we have shown that in the system styrene-isobutylene in the region of small amounts of the more active component, isobutylene, there is also observed a sharp increase in polymerization rate.

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SYNTHESIS AND PROPERTIES OF MIXED ESTERS OF PHENYLIMIDODITHIOCARBONIC ACID

A. I. Mashentsev

(Presented by Academician B. A. Kazansky, November 25, 1957)

The synthesis of new derivatives of carbon disulfide is of considerable interest in connection with the search for highly effective protective agents for plants.

Representatives of these materials have been used as fungicides, insecticides, and even herbicides. Such a broad spectrum of performance has a certain connection with the structural peculiarities and composition of the molecules of the various forms of carbon disulfide derivatives. The field of compounds to be considered is limited by the valence structure of carbon $=C\lesssim$, just as the field of organophosphorus insecticides is determined by the structure $=P\lesssim$; nevertheless, it can be asserted that the possibilities of synthesizing new compounds are far from exhausted, and the relationship of properties to composition and molecular structure is still not sufficiently clear.

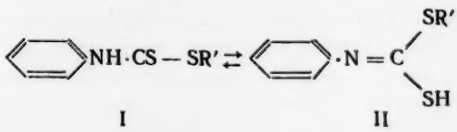
It is known that comparatively higher insecticidal activity frequently correlates with an unsymmetrical molecular structure, i. e., with a high dipole moment.

Therefore, a series of mixed esters of phenylimidodithiocarbonic acid was synthesized and characterized first. These esters correspond to the formula:

$$Ar-N=C\begin{matrix}SR'\\ \diagup\\ \diagdown\\ SR''\end{matrix},$$

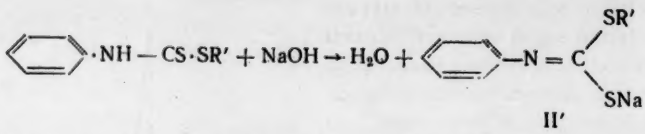
where R' and R" are different alkyl radicals, and Ar is a phenyl or more complex aryl group. The have not been described in the literature.

One of the available routes for the synthesis of similar esters is by alkylation of the corresponding dithiourethans. Most probably, one of the tautomeric forms of the dithiourethans [1-3] — form II — is alkylated; this form is quite characteristic for aromatic substituted dithiourethans:



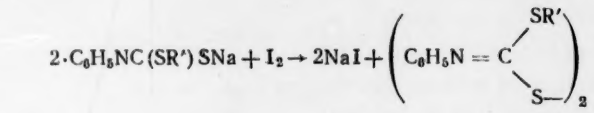
I II (1)

As our experiments showed, the equilibrium of a mixture of both (I and II) tautomeric forms is completely shifted toward the side of the ester-salt of the phenylimidodithiocarbonic acid (II') in the presence of an equivalent amount of alkali:



II′ (2)

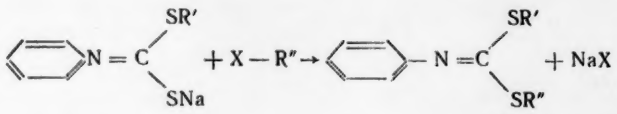
The formation of ester-salt (II′) is accompanied by migration of the hydrogen from the amino nitrogen and its conversion to an ionic state. The ester-salts of the alkali metals are comparatively stable; they are readily soluble in alcoholic and aqueous media. Oxidation of these solutions with iodine gave diphenyldialkylisothiuram disulfides, the formation of which is possible only from the imide form (II′) of the dithiourethan according to the equation:



(3)

In contrast to this, dithiourethans in form (I) are insoluble in water, and apparently do not participate directly in alkylation reactions.

Alkylation of the ester-salts in alcoholic media gives mixed esters of the desired composition in high yields and under mild reaction conditions. The latter circumstance is of considerable value, since the initial dithiourethans frequently are thermally unstable. The synthesis was carried out in an alcoholic solution of the dithiourethan containing the calculated amount of alkali or sodium alcoholate according to Equations (2) and (4):



(4)

where X is halogen (Cl, Br, or I). Thus, the reaction components were used in equimolar ratio. Usually, the reaction mixture was heated and stirred after the introduction of the alkyl halide. The reaction mixture was then allowed to stand protected from the atmosphere. Dilution with water liberated an oil, which was separated; the alcohol and the precipitated alkali metal halide went into the water layer. After the oily material had been washed repeatedly with water and dried, the individual ester was isolated by distillation under vacuum. Thus, the alkylation of the methyl ester of phenyldithiocarbamic acid with ethyl iodide, allyl bromide or chloride, n-propyl and isopropyl bromide, and n-butyl and isobutyl bromide was studied under comparable conditions. The physical constants and yields of the subtances prepared are presented in Table 1. The alkylation of the ethyl and allyl esters of phenyldithiocarbamic acid with methyl iodide was studied under the same conditions. The yields of compounds Nos. 1 and 2 (see Table 1) were practically the same as the yields obtained by the first variant of the synthesis. The mixed esters of phenylimidodithiocarbonic acid are colorless, transparent, viscous liquids with a characteristic odor. They are readily soluble in ether, benzene, and other organic solvents, but are insoluble in water. They hydrolyze with difficulty on long heating with water. On refluxing with acidic solutions of salts of heavy metals, they form characteristic precipitates of mercaptides.

TABLE 1

Expt. No.	Formula	M	B.p., °C/mm Hg	d_{20}^{20}	n_D^{20}	MR_D found	MR_D calc.	Yield, %
1	$\begin{matrix}C_2H_5S\\CH_3S\end{matrix}>C=NC_6H_5$	211.34	176/17	1.134	1.6185	64.79	64.80	78
2	$\begin{matrix}C_3H_5S\\CH_3S\end{matrix}>C=NC_6H_5$	223.35	185/17	1.131	1.6223	68.94	69.53	67
3	$\begin{matrix}n\text{-}C_3H_7S\\CH_3S\end{matrix}>C=NC_6H_5$	225.37	183/17	1.111	1.6065	69.41	69.70	84
4	$\begin{matrix}i\text{-}C_3H_7S\\CH_3S\end{matrix}>C=NC_6H_5$	225.37	175/17	1.153	1.6040	69.41	67.25	56
5	$\begin{matrix}n\text{-}C_4H_9S\\CH_3S\end{matrix}>C=NC_6H_5$	239.40	194/17	1.087	1.5953	74.02	75.01	81
6	$\begin{matrix}i\text{-}C_4H_9S\\CH_3S\end{matrix}>C=NC_6H_5$	239.40	186/17	1.091	1.5956	74.02	74.62	73

EXPERIMENTAL

1. Ethyl methyl ester of phenylimidodithiocarbonic acid. In a 150-ml three-necked flask, fitted with a stirrer, a reflux condenser, a thermometer, and a dropping funnel, was placed 40 ml of methanol, and 2.5 g of metallic sodium and 20 g of the methyl ester of phenyldithiocarbamic acid were successively dissolved in the methanol. 17 g of ethyl iodide was added to the colorless solution while stirring and cooling with water as required. A suspension and, later, a precipitate of sodium iodide gradually formed in the initially transparent solution. Liberation of heat occurred at the same time. Cooling for one and a half hours was succeeded by heating at 40-50° for two hours on a water bath. The reaction mixture was allowed to stand while sealed up. After two days, the resulting oil was repeatedly washed with water to a negative test for halogen ion, and was then dried over sodium sulfate; 21.8 g of product was obtained. The substance distilled at 175-177° and a pressure of 17 mm of mercury. 18.1 g (78.7% yield) was collected.

Found %: N 6.68; 6.71; S 30.12; 30.25. $C_{10}N_{13}NS_2$. Calculated %: N 6.63; S 30.34.

The density, refractive index, and molar refraction are presented in Table 1.

The other mixed esters were prepared similarly.

2. Allyl methyl ester of phenylimidodithiocarbonic acid. To a solution of 2.76 g of sodium in 44 ml of methanol were successively added 22 g of methyl phenyldithiocarbamate and 14.5 g of allyl bromide. 24.1 g of an oily material, which distilled at 184-186° (17 mm), was obtained. The yield was 17.9 g or 66.8%.

Found %: N 6.23; 6.44; S 28.52; 28.59. $C_{11}H_{13}NS_2$. Calculated %: N 6.27; S 28.71.

3. n-Propyl methyl ester of phenylimidodithiocarbonic acid. From a solution of 3.5 g of sodium in 56 ml of methanol, 28 g of the methyl ester of phenyldithiocarbamic acid, and 18.8 g of n-propyl bromide was obtained 29.5 g of a substance which distilled at 182 to 184° (17 mm). The yield of ester was 28.3 g or 83.7%.

Found %: N 6.51; 6.42; S 28.31; 28.38. $C_{11}N_{15}NS_2$. Calculated %: N 6.23; S 28.45.

4. Isopropyl methyl ester of phenylimidodithiocarbonic acid. From a solution of 2.52 g of sodium and 20 g methyl phenyldithiocarbamate in 40 ml of anhydrous methanol and 13.5 g of isopropyl bromide was obtained 19.8 g of material. Distillation from 173.5-175-5° (17 mm) gave a yield of ester of 13.6 g or 56.2%.

Found %: N 6.43; 6.39; S 28.52; 28.39. $C_{11}H_{15}NS_2$. Calculated %: N 6.23; S 28.45.

5. n-Butyl methyl ester of phenylimidodithiocarbonic acid. From 18 g of the methyl ester of phenyldithiocarbamic acid, 13.5 g of n-butyl bromide, and a solution of 2.26 g of sodium in 36g of methanol was isolated 23.2 g of material. After distillation from 193 to 195° (17 mm), the yield of ester was 19 g or 81.2%.

Found %: N 5.91; 5.74; S 26.65; 26.48. $C_{12}H_{17}NS_2$. Calculated %: N 5.86; S 26.78.

6. Isobutyl methyl ester of phenylimidodithiocarbonic acid. From a solution of 3.02 g of sodium, 24 g of the methyl ester of phenyldithiocarbamic acid, and 18 g of isobutyl bromide in 48 ml of anhydrous methanol was obtained 27.7 g of material distilling at 184.5 to 187.5° (17 mm). The yield was 22.8 g or 73.1%.

Found %: N 6.11; 6.03; S 2651; 26.45. $C_{12}H_{17}NS_2$. Calculated %: N 5.86; S 26.78.

Insecticidal properties of the mixed esters

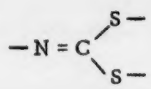
Tests, carried out over the last two years in the Institute of Zoology and Phytopathology of the Ministry of Agriculture, showed that the mixed esters of phenylimidodithiocarbonic acid are highly active as fumigants against various pests which attack agricultural crops, including pests which infest the soil. We present some representative data from a series of experiments.

Thus, after a 3-hour exposure at a concentration of 15 mg/liter, the per cent kill of granary weevils at the second and seventh days increased as follows: carbon disulfide, 0 and 57; dichloroethane, 0 and 65; ester

No. 6 (see Table 1), 0 and 87; ester No. 3, 52 and 94; ester No. 4, 25 and 100;* ester No. 2, 50 and 100; ester No. 5, 66 and 100; ester No. 1, 100 and 100; this shows their high activity as fumigants in comparison with such materials as carbon disulfide and dichloroethane.

The nematocidal activity against the potato nematode (Heterodera rostochiensis) of ester No. 1 was higher than that of the ethyl ester of dimethyldithiocarbamic acid. After the introduction of ester No. 1 as a dust in an amount of 30 grams of active principle per sq. m. of soil highly infected with nematodes, there were no cysts on the potato roots, and the larva population was zero, while in a standard test, there was 1 cyst on the roots and the larva population was 31.

Thus, high insecticidal activity was found for certain of the derivatives of carbon disulfide having in the molecule the group



All members of the series of mixed esters of phenylimidodithiocarbonic acid displayed some phytotoxicity when applied as a spray; this was established by the formation of localized scorch at the point of application on the surface of a green leaf. Broadening of the scorch zone was observed for ester No. 2 as it penetrated into the plant.

N. S. Kurnakov Institute
of General and Inorganic Chemistry
N. D. Zelinskii Institute
of Organic Chemistry
Academy of Sciences USSR

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* For all esters, the active concentration was 1.5-2.0 mg/liter.

POLYMERIZATION AND COPOLYMERIZATION OF UNSATURATED ORGANOSILICON COMPOUNDS. p-TRIALKYLSILYLSTYRENES

Corresponding Member AN SSSR V. V. Korshak, A. M. Poliakova, A. A. Sakharova, Corresponding Member AN SSSR A. D. Petrov and E. A. Chernyshev

The most important factors determining the ability of substituted ethylenes to polymerize are the number, nature, mutual disposition, and size of the substituents on the doubly-bonded carbon atoms [1].

We have previously shown [2] that trialkylvinylsilanes or, as they may also be named, trialkylsilylethylenes, $R_3SiCH=CH_2$, can be polymerized by a radical mechanism with the formation of viscous products having a polymerization coefficient of 12-18. The introduction of a second substituent in the β-position of this molecule leads to a considerable decrease or to the complete suppression of the ability to polymerize. Thus, for example, 1-triethylsilyl-2-methylethylene, $(C_2H_5)_3SiCH=CH-CH_3$, and 1,2-bis(triethylsilyl) ethylene, $(C_2H_5)_3SiCH=CHSi(C_2H_5)_3$, polymerize only to the dimers [3], and 1-dimethylpropylsilyl-2-phenylethylene, $(CH_3)_2C_3H_7SiCH=CH-C_6H_5$, is devoid of the ability to polymerize [2]. Substitution of the R_3Si-C$_6$H$_4$- group for the R_3Si group in the vinylsilylane molecule leads to the formation of the compound $R_3SiC_6H_4CH=CH_2$, which readily polymerizes into a vitreous product [4].

The introduction of a methyl group into the α-position of this molecule must bring about a decrease in its ability to polymerize, since the substitution causes steric hindrance. Actually, as established in the present investigation, p-triethylsilyl-α-methylstyrene, $R_3SiC_6H_4C(CH_3)=CH_2$, although it polymerizes by a radical mechanism to a glass, requires the use of pressure.

Thus, the ability of silicoolefins to polymerize is determined by the same factors as are determining in the case of unsaturated hydrocarbons.

We have previously published papers [2-4] presenting considerable material relating to the preparation of low-molecular-weight, oily polysilanes. The present investigation is devoted to the preparation of high-molecular-weight polysilanes and to a study of their properties. The polymerization of p-trialkylsilylstyrenes, $R_3SiC_6H_4CH=CH_2$, where $R=CH_3$ and C_2H_5, and of p-triethylsilyl-α-methylstyrene and the copolymerization of p-triethylsilylstyrene with styrene were investigated under standard conditions – atmospheric and 6000 atmospheres pressure and in the presence of 1% initiator. While the previously studied alkylalkenylsilanes [2-4] required the use of pressure for the formation of polymers, the p-trialkylsilylstyrenes polymerized under the same conditions but at atmospheric pressure. However, the use of pressure in the present case leads to a considerable increase in the molecular weight of the polymers (Table 1). We established, also, that p-triethylsilyl-α-methylstyrene polymerizes under a pressure of 6000 atm. to a solid product of lower molecular weight and at a lower rate than does p-triethylsilylstyrene. The intrinsic viscosities [η] of toluene solutions of the polymers of p-triethylsilylstyrene and of p-triethylsilyl-α-methylstyrene were, respectively, 0.784 and 0.460.

The results of the investigation of the copolymerization of p-triethylsilylstyrene with styrene showed that both with and without applied pressure, the resulting copolymer had a ratio of p-triethylsilylstyrene units to

styrene units of 1 : 2, and the intrinsic viscosities of the products formed under pressure and at atmospheric pressure were, respectively, 1.515 and 0.818.

TABLE 1

Polymerization of p-Triethyl- and p-Trimethylsilylstyrenes and of p-Triethylsilyl-α-methylstyrene

Expt. No.	Monomer (name and formula)	Polymerization conditions • pressure, atm.	temp °C	initiator ••	Yield reprecip. polymer, % of monomer	Outward appearance of polymer	[η] 100 ml/g	Found, % C	H	Si
1	p-Triethylsilylstyrene $(C_2H_5)_3SiC_6H_4CH=CH_2$	6000	120	TBP	75.4	Colorless glass	0.784	77.30 77.40	10.20 10.32	12.52 12.65
2	p-Triethylsilylstyrene	1	120	Same	62.0		0.241	77.40	10.38	12.27
3	p-Triethylsilylstyrene	6000	120	ABN	52.0		1.370	77.24	10.32	12.21
4	p-Triethylsilylstyrene	1	80	Same	47.3		0.133			
5	p-Trimethylsilylstyrene $(CH_3)_3SiC_6H_4CH=CH_2$	6000	120	TBP	67.0		1.22	75.24 75.27	9.36 9.42	15.29 15.49
6	p-Trimethylsilylstyrene	1	120	Same	60.0		0.324			
7	p-Triethylsilyl-α-methylstyrene $(C_2H_5)_3SiC_6H_4C(CH_3)=CH_2$	6000	120	Same	49.4		0.46	77.11 77.23	10.57 10.46	12.85 12.52

•Duration of experiment – 6 hours.

••Amount of initiator used was 1 mole %; TBP – tertiary butyl peroxide, ABN – azobisisobutyronitrile.

Thermomechnical tests were carried out on the polymerization and copolymerization products, and these tests showed that the p-triethylsilylstyrene polymer had a higher second order transition temperature than polystyrene prepared under the same conditions; the p-triethylsilyl-α-methylstyrene polymer had a still higher second order transition temperature (Figure 1).

TABLE 2

Copolymerization of p-Triethylsilylstyrene with Styrene at 120° and in the Presence of 1 mole % • Tertiary Butyl Peroxide

Expt. No.	Polymerization conditions •• pressure, atm.	mole ratio of monomers	Copolymer yield, wt. % on mon. mix.	Nature of copolymer	[η] 100 ml/g	Found, % C	H	Si	Calc., % (on Si) C	H	n/m•••
1	6000	1 : 1	89.1	Colorless glass, difficultly soluble in benzene, readily soluble in butanol	1.515	83.21 84.03	9.32 9.35	6.70 6.67	84.44	8.98	2
2	1	1 : 1	88.9	Colorless glass, readily soluble in benzene	0.818	84.98 84.81	8.84 8.77	6.21 6.49	84.44	8.98	2

• With respect to the monomer mixture.

•• Duration of experiment – 6 hours.

••• n – number of styrene units in copolymer, m – number of p-triethylsilylstyrene units: $\frac{n}{m} = \frac{\frac{2806}{x} - M_2}{M_1}$, where M_2 is the mol. wt. of p-triethylsilylstyrene, M_1 – is the mol. wt. of styrene, x is the percentage Si content in the copolymer.

The thermomechanical curves of the polymers and copolymers prepared are presented in Figure 1.

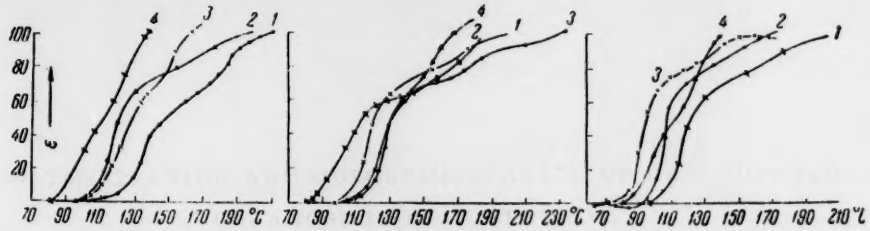

Fig. 1. Variation of deformation with temperature for the polymer samples. Left: 1 – p-triethylsilyl- α-methylstyrene polymer prepared under pressure with tertiary butyl peroxide; 2 – p-triethylsilylstyrene polymer prepared under the same conditions; 3 – same polymer prepared at atmospheric pressure; 4 – polystyrene prepared at atmospheric pressure. In center: 1 – p-triethylsilylstyrene polymer prepared under pressure with tertiary butyl peroxide; 2 – p-triethylsilylstyrene polymer prepared under pressure with azobisisobutyronitrile; 3 – p-trimethylsilylstyrene polymer prepared under pressure, 4 – p-trimethylsilylstyrene polymer prepared at atmospheric pressure. Right: 1 – p-triethylsilylstyrene polymer prepared under pressure in the presence of tertiary butyl peroxide; 2 – copolymer of p-triethylsilylstyrene with styrene prepared under the same conditions; 3 – copolymer of p-triethylsilylstyrene with styrene prepared at atmospheric pressure; 4 – polystyrene prepared under pressure.

EXPERIMENTAL

The p-trialkylsilylstyrenes were prepared by a method previously developed by us [5]. We have previously described the technique used in the experiments at high pressure [6].

The experiments at atmospheric pressure were carried out in sealed glass tubes. In all cases, the monomer was distilled into the tube in a stream of nitrogen immediately before the experiment.

The initiators, tertiary butyl peroxide and azobisisobutyronitrile, were used in an amount of 1 mole %. The reactions were carried out for 6 hours at 120 and 80°. When tertiary butyl peroxide was used as the initiator, the polymerization product was a composite glass rod; when azobisisobutyronitrile was used, the polymer was in the form of a congealed foam. The polymerization products were purified by reprecipitation from benzene, and copolymer No. 1 (Table 2) from butanol; in both cases, methyl alcohol was used as the precipitant. The reprecipitated polymers and copolymers had the form of colorless powders.

The products were characterized by the viscosities of toluene solutions and by their thermomechanical properties. The viscosities were measured in an Ostwald viscosimeter at 20°. The intrinsic viscosities were determined graphically from the resulting data. The investigation of the thermomechanical properties was carried out with a Tsetlin apparatus [7] at a load of 100 g and with a plunger diameter of 4 mm. The experimental results are presented in Tables 1 and 2 and in Figure 1.

Institute of Heteroorganic Compounds
Academy of Sciences USSR
N.D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR

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EQUILIBRIUM OF THE CONDENSED PHASES IN THE SYSTEM NAPHTHALENE–THIONAPHTHENE

V. M. Kravchenko and I. S. Pastukhova

(Presented by Academician I. I. Chernaev, October 5, 1957)

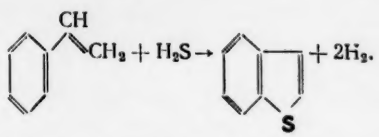
Naphthalene, which occupies second place, after benzene, among the cyclic products from the coking of coal, is separated from coal tar (by distillation, crystallization, and pressing) with admixed thionaphthene. The latter is removed by repeated washing with concentrated sulfuric acid, a final distillation, and by other methods.

The difficulties connected with the separation of thionaphthene from naphthalene have long been explained by the closeness of their physical properties, this leading, in particular, to the formation of solid solutions. However, a search of the literature down to the present time failed to reveal any data clearly characterizing the liquid-crystal phase equilibria in the system.

The article by H. G. Frank [1] gave only figures for the liquidus line, which permitted the construction of two intersecting curves from which it was possible to decide whether naphthalene and thionaphthene form a simple eutectic or solid solutions.

In an interesting monograph [2], W. Swietoslawski also considered the problem of the separation of thionaphthene from naphthalene, but he, too, failed to present any data on the phase equilibrium in this system. It was noted in reference [2] that the experimenters did not have pure thionaphthene at their disposal.

In solving the problem of the type of phase diagram possessed by the system naphthalene–thionaphthene, the first step was the careful preparation of the components. The thionaphthene was synthesized* by reacting styrene and hydrogen sulfide over a catalyst at a temperature of 600°.



After purification, the thionaphthene melted at a temperature of 31.2° (± 0.1°).

"Pure" naphthalene was freed from traces of thionaphthene by treatment with metallic sodium, distillation, and recrystallization; the resulting naphthalene melted at a temperature of 80.2° (± 0.1°).

The crystallization and melting processes were studied by the method of thermal analysis using a convenient laboratory apparatus [3], and a series of mixtures of the components was also investigated dilatometrically.

Our experimental results, which characterize the equilibrium of the condensed phases, are collected in Table 1. The temperature–composition diagrams, which were constructed from these data and which relate

* With the assistance of V. E. Mil'skii.

the composition (X) to the temperature of initial (t_1) and completed (t_2) crystallization, are shown in Figure 1. It was found that naphthalene and thionaphthene form a system of limited solid solutions with an eutectic. The minimum temperature of crystallization (melting) of the solid solutions was 29.9°, and the corresponding composition was 5.8 mole % (5.60 wt. %) naphthalene and 94.2 mole % (94.40 wt. %) thionaphthene.

TABLE 1

The System Thionaphthene–Naphthalene

Amt of thionaphthene		Amt of naphthalene		t_1, °C	t_2, °C
wt. %	mole%	wt.%	mole%		
100.0	100.0	0.00	0.0	31.2	31.2
97.82	97.7	2.18	2.3	31.0	—
95.90	95.7	4.10	4.3	30.2	30.1
94.40	94.2	5.60	5.8	29.9	29.9
92.05	91.7	7.95	8.3	30.3	30.0
90.04	89.6	9.96	10.4	31.9	30.1
85.10	84.5	14.90	15.5	35.3	30.1
78.29	77.5	21.71	22.5	39.7	30.3
71.41	70.5	28.59	29.5	43.8	30.5
63.84	62.8	36.16	37.2	48.6	—
60.30	59.2	39.70	40.8	50.2	37
53.88	52.8	46.12	47.2	54.2	44
46.39	45.2	53.61	54.8	58.5	50
36.77	35.7	63.23	64.3	64.0	56
26.22	25.4	73.78	74.6	68.8	—
16.47	15.8	83.53	84.2	72.9	70
8.96	8.6	91.04	91.4	76.5	—
4.91	4.7	95.09	95.3	78.1	—
0.00	0.0	100.00	100.0	80.2	80.2

Crystallization proceeded with very little lag on cooling of the melted and vigorously stirred mixtures. Supercooling of the solid solutions on the naphthalene side was 0.5-1°, and that on the thionaphthene side was 1.5-2°.

The ideal solubility curves for the system, plotted as broken lines in Figure 1, were calculated by means of the equation of I. F. Shreder [4]: $\ln X = Q(1/T_1)/R$, where Q (cal./mole) is the heat of fusion, T is the absolute temperature at which the solution is saturated with X mole fraction, and R is 1.987 cal./mole. In the calculation, the heat of fusion of naphthalene was taken as Q = 4610 cal./mole [5], determined calorimetrically on a naphthalene sample melting at 80.0°, and the heat of fusion of thionaphthene was taken as Q = 2826.8 cal./mole [6]. It is seen from Figure 1 that the ideal solubility curves and the experimental t–X diagram diverge considerably. The experimental eutectic point is shifted above the ideal eutectic (e) by $\Delta t \approx 14°$ and toward the thionaphthene side by $\Delta X \approx 17$ mole %. Such a considerable deviation of these points can be explained by the formation of naphthalene-thionaphthene solid solutions having a liquidus line which tends toward a straight line (cf. the analogous situation in [7]).

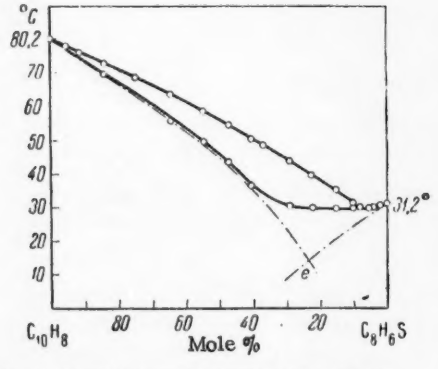


Fig. 1. Liquid–crystal equilibrium in the system naphthalene–thionaphthene.

Averaged structural data for naphthalene [8] indicate equal C–C bond lengths of 1.4 A and equal valence bond angles ∠ C – C=C of 120°. By supplementing these data with values for the van der Waals radii R_C = 1.72 A and R_H = 1.17 A, it is possible to calculate the sectional area of a planar model of naphthalene, which turns out to be $S \approx 50$ A^2.

In a recent paper [9], values of 1.354 to 1.421 C – C and valence angles ∠C – C=C from 119 to 121° were given for naphthalene. The question arises as to how these new data would change the value of S for the naphthalene molecule at constant R_C and R_H. Calculation showed that the order of magnitude of ΔS is less than 1 A^2 (in a similar case of anthracene, taking R_C = 1.72 A and R_H = 1.17 A, $\Delta S \approx 0.4$ A^2 [10]).

As before [10, 11], such a small change in the value of S permits the use of averaged structural data for the construction of the cross sections (S and S') of the molecular model of naphthalene (Figure 2).

We found nothing in the literature on the characteristics of the structure of thionaphthene. An approximate construction of a cross section of its model (S_1 and S_1') is presented in Figure 2; the construction was carried out by a combination of a single six-membered ring of naphthalene with the five-membered ring of thiophene (the latter has been studied [12]). The following values for thiophene were used [11]: C'–C" = 1.35 A, C–C = 1.44 A, C–S = 1.74 A, C – H = 1.08 A, ∠C – S–C = 91°, ∠S – C'– C" = 112°, ∠C'– C" – C=113° [11]. The van der Waals radii in Figure 2 are: R_C = 1.72 A, R_H = 1.17 A, R_S = 1.85 A.

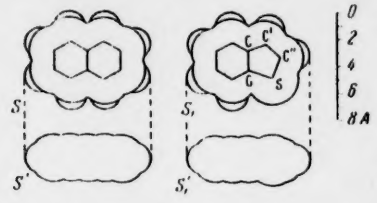


Fig. 2. Cross sections of schematic models of the molecules of naphthalene (S and S') and thionaphthene (S_1 and S_1').

The ratio of the larger cross sections of the molecular models is $S/S_1 \approx 5\%$; when S is superimposed on S_1, the latter is completely circumscribed. On comparison of the smaller cross sections of the models, S' and S_1', it is seen that the sulfur atom of the thionaphthene extends only insignificantly beyond the boundary of the corresponding part of the contour of the naphthalene molecule.

The noted small deviations in the dimensions and forms of the cross sections of the molecular models of naphthalene and thionaphthene explain the limited isomorphism which occurs in these substances.

Over the largest part (40-100% naphthalene) of the t–X diagram in Figure 1, the points on the liquidus line coincide with the limiting straight line which can be drawn between the melting points of the pure components. In the smaller part (0-40% naphthalene) of the t–X diagram there is observed a slight deviation of the liquidus curve from the straight line; this deviation does not exceed 5° at the minimum point. This portion of the t–X diagram, which corresponds to a relatively increased content of thionaphthene, can be explained by the specific effect of the latter – by the effect of the sulfur heteroatoms, which differ in dimensions and force fields from the CH groups in the molecules of the components of the solid solution.

N. S. Khrushchev Donets
Industrial Institute

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REACTIONS OF DIFERROCENYLMERCURY

Academician A. N. Nesmeianov, E. G. Perevalova

As has already been shown, mercury derivatives of ferrocene [1], which were first prepared by us, can be used for the synthesis of ferrocene derivatives. Thus, they react with halogens (iodine and bromine) to yield the corresponding halide compounds. We have prepared haloferrocenes by this method [2].

In the present work, we reacted diferrocenylmercury with triphenylchloromethane, with carbonyl and sulfonyl halides, with thiocyanogen (nascent), and with selenium tetrabromide.

Diferrocenylmercury reacts with triphenylchloromethane under very mild conditions to give a small amount of ferrocene and ferrocenyltriphenylmethane in a yield of 18% of theoretical:

$$(C_5H_5FeC_5H_4)_2Hg + 2\,(C_6H_5)_3CCl \rightarrow 2C_5H_5FeC_5H_4C\,(C_6H_5)_3 + HgCl_2.$$

The reaction proceeds more difficultly with sulfonyl chlorides. Thus, heating diferrocenylmercury with ferrocenesulfonyl chloride and benzenesulfonyl chloride in benzene solution yields diferrocenyl sulfone and phenyl ferrocenyl sulfone in 5-6% yield. In addition, 35-38% of the diferrocenylmercury is converted to ferrocene.

$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow{C_5H_5FeC_5H_4SO_2Cl} (C_5H_5FeC_5H_4)_2SO_2$$
$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow{C_6H_5SO_2Cl} C_5H_4FeC_5H_4SO_2C_6H_5$$

The reaction with acetyl chloride proceeds still more difficultly. Acetylferrocene is obtained in only 1% yield, and a considerable part of the diferrocenylmercury is converted to ferrocene. Diferrocenylmercury does not react with benzoyl chloride.

As would be expected, the reaction with sulfonyl iodides proceeds considerably more readily than the reaction with sulfonyl chlorides. Thus, in the reaction of diferrocenylmercury with benzenesulfonyl iodide, the yield of phenyl ferrocenyl sulfone is 22%.

The reaction of diferrocenylmercury with an excess of thiocyanogen yields a complex, and treatment of the complex with an aqueous solution of sodium thiosulfate yields diferrocenyl disulfide in a yield of 15% calculated on the reacted mercury compound (12% of the diferrocenylmercury was recovered unchanged):

$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow{(CNS)_2} [C_5H_5FeC_5H_4SCN] \xrightarrow{Na_2S_4O_6} C_5H_5FeC_5H_4 - S - S - C_5H_4FeC_5H_5.$$

It is probable that the initially formed thiocyanoferrocene is reduced to the disulfide by the action of the sodium thiosulfate; moreover, 25% of the reacting diferrocenylmercury is converted to ferrocene.

The reaction of diferrocenylmercury with $SeBr_4$ yields diferrocenylselenium in 21% yield, the selenium being reduced to the divalent state during the process; this reduction can occur by oxidation of the iron in the ferrocenyl group or during the subsequent treatment of the reaction mixture with sodium thiosulfate:

$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow[(Na_2S_2O_3)]{SeBr_4} (C_5H_5FeC_5H_4)_2Se.$$

It should be noted that in all cases the reaction product is completely or partially in the oxidized (ferrocenonium) form, and is then reduced with sodium thiosulfate.

Thus, the high nucleophilic activity of the carbon atoms in ferrocene, which is apparent in the ease of electrophilic substitution of the hydrogens of the cyclopentadienyl rings, is also observed in mercury derivatives of ferrocene; diferrocenylmercury reacts with sulfonyl halides under milder conditions than does diphenylmercury [3, 4]. The reaction of triphenylchloromethane with diphenylmercury has not been reported.

It should be noted that ferrocene was isolated as a by-product in all of the reactions investigated (except the reaction with $SeBr_4$). It is possible that the formation of ferrocene is due to the emergence of a ferrocenyl radical which captures a hydrogen from the solvent or from the other ferrocenyl groups.

EXPERIMENTAL

Preparation of ferrocenyltriphenylmethane. 1.9 g (0.0068 mole) of triphenylchloromethane was added to a suspension of 1.9 g (0.0033 mole) of diferrocenylmercury in benzene. Over a period of several minutes, the orange color of the ferrocenylmercury changed to the rose color characteristic of complexes of ferrocene with mercuric chloride. The reaction mixture was refluxed for 4 hours, during which time the suspended material changed from rose to green. The benzene was distilled. The residue was treated with a saturated aqueous solution of sodium thiosulfate. The precipitate was filtered and extracted with ether. The ether was distilled, the remaining material was dissolved in petroleum ether, and the mixture was resolved by chromatographing in an Al_2O_3 column. Elution of the column was with petroleum ether. This separation gave 0.01 g of ferrocene (about 1% of the diferrocenylmercury was converted to ferrocene), an insignificant amount of an unidentified oily material, and 0.5 g of ferrocenyltriphenylmethane which melted at 179-181°, after recrystallization from n-butyl alcohol. The yield was 18% of theoretical (in all cases, the yield in per cent of theoretical was calculated on the basis of both ferrocenyl groups in the diferrocenylmercury). The ferrocenyltriphenylmethane was readily soluble in benzene and somewhat less soluble in alcohol and ether.

Found %: C 81.08; 81.00; H 5.78; 5.82. $C_{29}H_{24}Fe$. Calculated %: C 81.31; H 5.65.

Preparation of phenyl ferrocenyl sulfone. An excess of a benzene solution of benzenesulfonyl iodide was added to 4.8 g (0.0084 mole) of diferrocenylmercury. The reaction mixture was allowed to stand overnight, and was then treated with a saturated aqueous solution of sodium thiosulfate. The filtrate was filtered and extracted with benzene. The benzene solutions were combined and chromatographed over Al_2O_3.

0.5 g of ferrocene (apparently contaminated with iodoferrocene), 0.9 g of phenyl ferrocenyl sulfone, and 1.3 g (27%) of the original diferrocenylmercury were isolated.

The phenyl ferrocenyl sulfone was recrystallized from alcohol. M.p. 145-146°. The yield was 22% calculated on the reacted diferrocenylmercury.

Found %: C 59.30; 59.16; H 4.48; 4.44; S 9.57; 9.48; Fe 16.96; 17.08. $C_{16}H_{14}SO_2Fe$. Calculated %: C 58.91; H 4.32 S 9.83; Fe 17.12.

Preparation of diferrocenyl sulfone. 1.6 g (0.0028 mole) of diferrocenylmercury and 1.6 g (0.0056 mole) of ferrocenylsulfonyl chloride were heated in absolute benzene at the boiling point for 18 hours. Further treatment of the reaction mixture was as described for phenyl ferrocenyl sulfone.

There were obtained 0.35 g of ferrocene (35% yield), 0.48 g of the original ferrocenesulfonyl chloride (30% of that used in the reaction; moreover, part of the sulfonyl chloride was converted to the acid in the chromatographic column), 0.1 g of diferrocenyl sulfone, and 0.02 g of ferrocenylmercury chloride.

The diferrocenyl sulfone was recrystallized from butyl alcohol. The yield was 6% calculated on the reacted ferrocenesulfonyl chloride. M. p. 270-275° with decomposition.

Found %: C 54.99; 55.20; H 4.07; 4.24; S 6.83; 6.71; Fe 26.44; 26.45. $C_{20}H_{18}SO_2Fe_2$. Calculated %: C 55.33; H 4.18; S 7.38; Fe 25.73.

The reaction with benzenesulfonyl chloride was carried out by heating for 13 hours. The yield of phenyl ferrocenyl sulfone was 5% of theoretical. 38% of the diferrocenylmercury was converted to ferrocene.

Reaction of diferrocenylmercury with acetyl chloride. 0.25 ml (0.0035 mole) of acetyl chloride was added to a suspension of 1 g (0.0017 mole) of diferrocenylmercury in absolute benzene. The reaction mixture

was refluxed for 5 hours, the benzene was then distilled and the dark, solid residue was reduced with a saturated aqueous solution of sodium thiosulfate and then extracted with ether. After distillation of the ether, the residue was added to the benzene solution. The benzene solution was diluted two-fold with petroleum ether, and ferrocene (1.05 g) and acetylferrocene were isolated from it by chromatographic adsorption over aluminum oxide.

94% of the original diferrocenylmercury was converted to ferrocene. The yield of acetylferrocene was 0.01 g (1.1% of theoretical). The m. p. of the recovered material and of a mixed sample was 82-84°.

It was not possible to prepare benzoylferrocene under similar conditions; 80-95% of the diferrocenylmercury was recovered unchanged.

Preparation of diferrocenyl disulfide. 4 g (0.007 mole) of diferrocenylmercury was ground in a mortar with an alcoholic solution of thiocyanogen, which was prepared by alcoholic extraction of a mixture of equivalent amounts of $CuSO_4$ and KSCN which had been ground in a mortar. The addition of the alcoholic solution of thiocyanogen and the grinding were continued until the solution was decolorized. The reaction mixture was then heated with stirring for 10-15 minutes; during the heating, an alcoholic solution of thiocyanogen (approximately 20 ml) was added several times until the color no longer changed. The reaction mixture was poured into a saturated aqueous solution (150 ml) sodium thiosulfate, and, after 3 hours, the mixture was diluted with water until the resulting precipitate no longer formed (800-900 ml of water was added). The filtered precipitate was extracted with ether. The insoluble portion (0.5 g) was unchanged diferrocenylmercury (m.p. of this material and of a mixed sample was 232-233°.

The substance was dissolved in petroleum ether, and separated in a chromatographic column packed with Al_2O_3. Ferrocene (0.6 g) was eluted from the column with petroleum ether. 25% of the diferrocenylmercury was converted to ferrocene.

Elution was then continued with a mixture of petroleum ether and benzene in a ratio of 2 : 1. After distillation of the solvent, there remained a yellow crystalline material and a small amount of an oily product; the latter was carefully washed with ether, but was not further investigated. The remaining crystalline material (0.4 g) was diferrocenyl disulfide. The yield was 15% calculated on the reacted diferrocenylmercury. After recrystallization of the disulfide from n-butyl or ethyl alcohol, the m. p was 185-187°.

The diferrocenyl disulfide was readily soluble in benzene and less soluble in ether and petroleum ether.

Found %: C 55.12; 55.09; H 4.12; 4.12; S 14.68; 14.50. $C_{20}H_{18}S_2Fe_2$. Calculated %: C 55.32; H 4.18; S 14.76.

Preparation of diferrocenylselenium.* A solution of 8.3 g (0.0415 mole) of $SeBr_4$ in 250 ml of $CHCl_3$ was added, with stirring, to a suspension of 5 g (0.0092 mole) of diferrocenylmercury in $CHCl_3$. The mixture was heated at the boiling point for 1 hour. The red chloroform solution was then decanted. The dark residue was ground in a mortar, and treated with a saturated aqueous solution of sodium thiosulfate. After several days, the aqueous layer and the dark residue were repeatedly extracted with ether. The ether was distilled, and the remaining diferrocenylselenium (1.4 g) was recrystallized from isobutyl and ethyl alcohols. The yield was 0.8 g, 21% of theoretical. M. p. 151-153°.

Found %: C 53.22; 53.63; H 4.16; 4.40. $C_{20}H_{18}SeFe_2$. Calculated %: C 53.45; H 4.01.

M. V. Lomonsov Moscow
State University

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* The diferrocenylselenium was prepared by us together with Iu. L. Bakov.

THE REACTION OF VINYLACETYLENE WITH DIAZOMETHANE

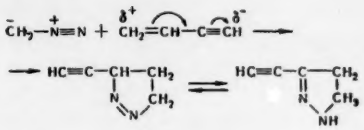
A. T. Troshchenko and A. A. Petrov

(Presented by Academician B. A. Arbuzov, December 2, 1957)

Certain basic regularities of the reactions of vinylacetylenic hydrocarbons with electrophilic reagents have been described in a series of published works from our laboratory [1, 2]. No less interesting are the reactions of these hydrocarbons with nucleophilic reagents. In the present article are considered the results of experiments on the reaction of vinylacetylene with a typical nucleophilic reagent – diazomethane [3, 4].

Diazomethane reacts readily with acetylene with the formation of pyrazole [5]. With ethylene, it gives pyrazoline, though in poor yield [6]. It reacts with butadiene to give either 5-vinylpyrazoline or 5,5'-dipyrazolyl [7] depending on the ratio of reactants and the reaction time; correspondingly, with diacetylene, it gives ethynylpyrazole or dipyrazolyl [8]. We did not find any data in the literature on the order of addition of diazomethane to vinylacetylene.

In connection with the great inclination of the triple bond toward the addition of nucleophilic reagents, it might be expected that diazomethane and vinylacetylene would form vinylpyrazole. However, our experiments showed that addition takes place only at the double bond, and the product of the reaction is 3-ethynylpyrazoline, in accordance with the scheme:



The structure of the substance obtained was demonstrated as follows.

1. 97.8% acetylenic hydrogen (terminal acetylenic grouping) was found by the mercury method [9].

2. The infrared spectrum of the substance (see Figure 1) had a rather intense band corresponding to a conjugated terminal acetylenic group (2100 cm^{-1}), an intense band corresponding to the CH vibration of the acetylenic group (3280 cm^{-1}), and a band at about 1700 cm^{-1} which is characteristic of acetylene [10]. Characteristic frequencies of the vinyl group in the 900-1000 cm^{-1} region were absent. An intense band at 1526 cm^{-1} corresponded to a double bond.

3. With the aim of determining the position of the double bond in the ring, we took the infrared spectrum of pyrazoline. A higher frequency at 1585 cm^{-1} corresponds to the double bond in this compound. Consequently, conjugation of the double and acetylenic bonds occur in our ethynylpyrazoline, since lower values of infrared frequencies have been assigned to both of these bonds.

Thus, as a result of the present investigation, it has been established that vinylacetylene reacts as a conjugated system with diazomethane, and it adds diazomethane only at the double bond. The order of addition agrees with the assumed polarization of vinylacetylene and with the nucleophilic nature of diazomethane.

EXPERIMENTAL

To an ethereal solution of diazomethane containing about 5 g of CH_2N_2 and cooled to −5° was added liquid vinylacetylene (3.9 g) in the form of an ethereal solution (20 ml of ether) cooled to the same temperature.

The mixture was allowed to stand in the dark at room temperature for 24 hours. The color of the solution faded somewhat; however, the fading was not complete (on longer standing, the color intensified).

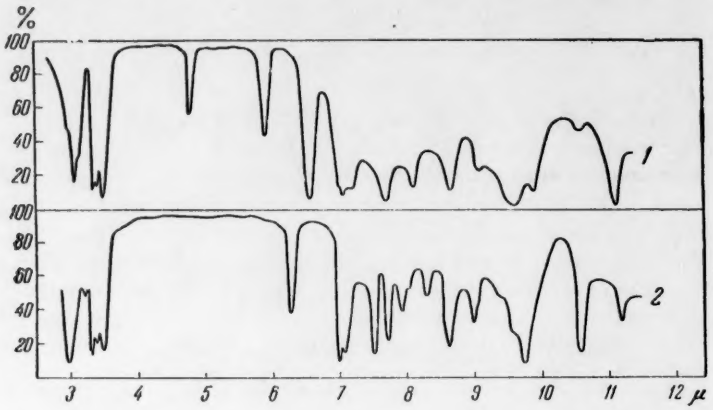


Fig. 1. Infrared transmission spectra: 1 – ethynylpyrazoline, 2 – pyrazoline.

The ethereal solution was filtered from the flocculent precipitate and freed from solvent by distillation on a water bath with a temperature of 40-50° (toward the end, the distillation was carried out under the vacuum of a water aspirator). From the residue was obtained an oil (6.3 g) which distilled under vacuum within a one-degree range. The yield was 89.5% of theoretical. B. p. 54-55°/5 mm, d_4^{20} 1.019, n_D^{20} 1.4830.

Found %: C 63.61; 63.67; H 6.44; 6.41; N 29.83. $C_5H_6N_2$. Calculated %: C 63.80; H 6.47; N 29.70.

The product was a colorless, transparent oil with a peculiar odor reminiscent of cocoa. Fine bubbles of a colorless gas were liberated on standing of the solution, and the color of the solution changed first to yellow and then to red. It imparted a yellow-red color to pine shavings. The product formed a red precipitate with Ilosvay's reagent and a light yellow precipitate with an ammoniacal solution of silver oxide.

The infrared spectrum (cm^{-1}): 899 v.s., 943 av. 1011 s, 1043 av., 1100 s, 1154 s, 1233 s, 1296 s, 1391 s, 1422 s, 1526 v. s, 1700 s, 2100 av., 2852 s, 2864 s, 2914 av., 2940 av., 2970 s, 3280 s, 3332 w.

The infrared spectrum of pyrazoline (cm^{-1}): 892 av., 940 s, 1028 av., 1115 av., 1158 s, 1204 s, 1258 av., 1290 s, 1328 s, 1404 s, 1433 s, 1585 s, 2869 s, 2950 s, 2975 s, 3090 av., 3322 av..

The infrared spectra were taken with an IKS-12 spectrophotometer with an LiF prism of 5μ and with an NaCl prism beyond 5μ.

Lensoviet Leningrad
Technological Institute

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THE USE OF ORGANOZINC COMPOUNDS FOR THE SYNTHESIS OF CARBON-CARBON DERIVATIVES OF SUGARS

Iu. A. Zhdanov, G. N. Dorofeenko and G. V. Bogdanova

(Presented by Academician A. I. Oparin, December 10, 1957)

As was shown previously [1, 4], the most satisfactory method for the synthesis of C–C derivatives of carbohydrates is the organomagnesium method, which is based on the interaction of acetylated sugar halides with a Grignard reagent. The method is simple and gives high yields of the desired products. However, a material drawback of the method is the necessity of introducing into the reaction a large excess of organomagnesium compound, since not only the halogen of the acetylated sugar reacts with it, but so do the acetyl groups.

Attempts have been made to obviate this drawback both through the use of methylated instead of acetylated sugars [5] and by substitution of the active organomagnesium compounds by the less active organocadmium compounds [6]. The use of this route encountered difficulties in the purification of the final products, and the yields of C–C derivatives were low. Attempts by us to prepare allyltetraacetylglucose by the interaction of acetochloroglucose with allylaluminum bromide ended unsuccessfully.

In view of the fact that organozinc compounds have very little tendency to interact with carbonyl groups and esters, it seemed of interest to use them for the synthesis of carbon-carbon derivatives of carbohydrates.

Heating of acetochloroglucose with a two-fold excess of phenyl- and p-anisylzinc chloride in toluene solution resulted in uncrystallizable, sirupy materials, from which we were able to isolate phenyltetraacetylglucose and p-anisyltetraacetylglucose in yields of up to 11 and 5%, respectively.

TABLE 1

Expt. No.	Mole ratio of acetochloroglucose to phenylzinc chloride	Heating time, hours	Yield of phenylacetylglucose, %	Unreacted acetochloroglucose, %	Amount of diphenylmethylcarbinol, g
1	1 : 9	10	2.5	7.3	4.02
2	1 : 2	10	4	17.8	3.18
3	1 : 2	6	8.5	18.5	2.51
4	1 : 2	4	11	27	1.8
5	1 : 2	3	5	65	1

A study of the by-products showed that incompletely substituted organozinc compounds react in part with the acetyl groups of the acetochloroglucose, forming considerable amounts of carbinols. The presence of unreacted acetochloroglucose and of an unsaturated carbohydrate, probably tetraacetyl-2-hydroxyglucal in this case, was established in all experiments. The yield of C–C derivative and the amount of by-products varied with the ratio of reactants and the reaction time, as illustrated by the data in Table 1 (10 g of α-acetochloroglucose was introduced into the reaction in each case).

Completely substituted organozinc compounds also react with acetochloromonoses to yield C–C derivatives of monoses. Phenylacetylglucose was prepared by this method in yields of up to 15%, as was phenyltriacetylarabinose.

Thus, we have demonstrated that it is possible, in principle, to prepare carbon-carbon derivatives of carbohydrates by the organozinc method; however, the yields of end products are lower than they are when organomagnesium compounds are used.

EXPERIMENTAL

Synthesis of phenyltetraacetylglucose by means of phenylzinc chloride. In a three-necked flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer, a solution of phenylmagnesium bromide was prepared from 1.32 g (0.055 mole) of magnesium and 9 g of bromobenzene in 30 ml of absolute ester, and 7.44 g (0.055 mole) of anhydrous zinc chloride in 12 ml of absolute ether was added gradually with stirring and cooling. Upon the addition of dry toluene to the solution, a suspension of phenylzinc chloride was formed. A solution of 10 g (0.027 mole) of acetochloroglucose in 25 ml of toluene was added to the suspension while stirring.

The mixture was heated on a boiling water bath in a stream of dry nitrogen, the optimum yield of phenyltetraacetylglucose being obtained with a reflux time of 4 hours.

After decomposition of the reaction mixture with water and dilution with acetic acid, the ether-toluene layer was separated from the water layer, washed with a saturated solution of sodium bicarbonate, and dried over anhydrous sodium sulfate. After distillation of the solvent under vacuum, 7.7 g of a light yellow sirup was obtained.

Quantitative analysis of the sirup for chlorine (lime method) showed that it contained 27% unreacted acetochloroglucose. The sirup readily added bromine and decolorized permanganate solution, which indicated the presence of an unsaturated carbohydrate.

Deacetylation was used to separate the phenylacetylglucose from the accompanying carbinols. For this purpose, a well chilled solution of the sirup in 30 ml of chloroform was added, with stirring and cooling, to a solution of 2 g of sodium in 50 ml of absolute methanol. The solution was stirred for 5 minutes, allowed to stand for half an hour in a freezing mixture, and then was acidified with dilute acetic acid to a weakly acid reaction. The resulting solution was extracted three times with chloroform. From the chloroform layer, after distillation of the solvent, was obtained pure diphenylmethylcarbinol (m.p. 77-78°) in an amount of 1.8 g.

The aqueous layer was evaporated to a sirup and acetylated by heating for 3 hours with 50 ml of acetic anhydride and 5 g of anhydrous sodium acetate. Further treatment was as during the ordinary organomagnesium synthesis. As a result, there was obtained 1.7 g of a thick sirup, from which, by recrystallization from isopropyl alcohol, was isolated 1.1 g (11% theoretical) of phenyltetraacetylglucose with a m. p. of 153-154°, after a second recrystallization. A mixture of this product with known phenyltetraacetylglucose melted in the same range. Oxidation with alkaline permanganate gave benzoic acid.

With the aim of eliminating the deacetylation step and the second acetylation, an experiment was carried out in which the phenylacetylglucose was separated from the by-products by chromatography. For this separation, the ether-toluene layer, obtained from the reaction of the phenylzinc chloride with the acetochloroglucose, was chromatographed in a column packed with calcined aluminum oxide. The aluminum oxide was eluted with 175 ml of benzene. After distillation of the solvent under vacuum, a light yellow sirup was obtained, which crystallized on pouring into cold isopropyl alcohol. 0.45 g (5% of theoretical) of phenylacetylglucose, m. p. 153-154°, was obtained. A mixed melting point showed no depression. Oxidation gave benzoic acid.

Preparation of anisyltetraacetylglucose. p-Anisylzinc chloride was prepared by the above-described method from 1.32 g of magnesium, 10.7 g of p-bromoanisole, and 7.44 g of zinc chloride. An ethereal solution of 10 g of acetochloroglucose was added to the organozinc compound, and the mixture was heated for 4 hours. After deacetylation and the usual treatment, 0.5 g (5% of theoretical) anisyltetraacetylglucose, m. p. 102°, was obtained. A mixed sample showed no melting point depression. Oxidation gave p-methoxybenzoic acid.

Synthesis of phenyltetraacetylglucose by means of diphenylzinc. Diphenylmercury, required for the synthesis of the diphenylzinc, was prepared by the diazo method of A. N. Nesmeianov [7]. The diphenylzinc was synthesized by refluxing a xylene solution of diphenylmercury with zinc powder [8]. A xylene suspension of diphenylzinc, prepared from 6 g (0.017 mole) of diphenylmercury and 4.8 g of zinc dust, was heated on a boiling water bath with 3 g (0.008 mole) of acetochloroglucose in 15 ml of benzene for 1.5 hours.

The reaction mixture was decomposed with dilute acetic acid. The xylene solution was separated, washed with water, and dried, and the solvent was then distilled under vacuum. The resulting viscous sirup was completely acetylated with acetic anhydride in the presence of anhydrous sodium acetate. The reaction mixture was poured into water. The aqueous solution was extracted with ether, and, after distillation of the ether, 2.8 g of a yellow sirup was obtained. The sirup was dissolved in the minimum amount of hot isopropyl alcohol. On prolonged standing of the solution in a refrigerator, 0.46 g (14% of theoretical) of phenyltetraacetylglucose, m. p. 151-152°, crystallized. A mixed sample showed no depression of the melting point. Oxidation of the material gave benzoic acid.

Preparation of phenyltriacetylarabinose. The reaction of diphenylzinc with acetochloroarabinose was carried out by the method described above. Ultimately, there was obtained a yellowish sirup, from which, by prolonged crystallization from isopropyl alcohol, was isolated some phenyltriacetylarabinose, m. p. 91-92°. A mixture with known phenyltriacetylarabinose melted without depression of the m. p.

Rostov-on-the-Don
State University

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INVESTIGATION OF THE PHASE COMPOSITION OF ALLOYS OF IRON WITH VANADIUM AND OF IRON WITH CHROMIUM

M. I. Zakharova, I. A. Ignatova, L. A. Semenova
and N. A. Khatanova

(Presented by Academician A. A. Bochvar, November 12, 1957)

According to the literature [1, 2], in the structural diagrams of iron–vanadium and iron–chromium alloys there is a σ-phase region which, at temperatures above 1234° for Fe–V alloys and above 820° for Fe–Cr alloys, is converted into a region of α-phase solid solutions. However, the sharp change in properties of the alloys inside the single-phase regions of both the σ- and the α- phases indicates a more complex nature for the phase transformations. Thus, for example, in alloys which belong, according to the structural diagram, to the single-phase σ-region, brittleness sharply appears after annealing at temperatures of 400-550°. At the same time, the plasticity falls to zero, which sets a limit on the practical use of the alloys. Lena and Hawkes [3] consider that strengthening of Fe–Cr alloys at low annealing temperatures is explained by the separation of a solid solution rich in chromium. A similar point of view is held by Williams and Paxton [4], who, on the basis of their experimental investigation, concluded that there are two eutectoid reactions in the system Fe–Cr at temperatures below 600°.

A change in properties not corresponding to a single-phase solid solution has also been observed [6, 7] at temperatures above the transition temperature of the σ- to the α-phase. This change in properties is difficult to explain by a process involving ordering of the atoms, which has been proposed by some investigators for both low and high temperatures [7].

The aim of the present investigation was to study the structures of iron–vanadium and iron–chromium alloys after heating at various temperatures in the interval 1400-600° with subsequent quenching in water.

The alloys were prepared from electrolytic iron, electrolytic chromium, vanadium reduced from vanadium oxide and containing 99.6% V and 0.08% C, and from aluminothermic vanadium containing ~1% Si.

The alloys of Fe with 49.5 atom % V and Fe with 50 atom % Cr were prepared without the use of crucibles. The alloys of Fe with 28.5, 43, and 74 atom % V and of Fe with 35, 42, and 48 atom % Cr were prepared from vanadium containing Si as an impurity.

The investigation was carried out by means of the powder method of x-ray analysis and by microscopic analysis. The alloys were homogenized, after casting, at a temperature of 1300° for 20 to 100 hours, and were quenched from these temperatures in water.

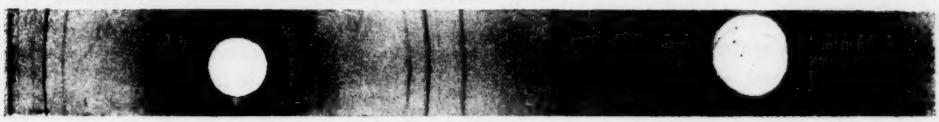

Fig. 1. Diffraction patterns of iron alloy containing 42% chromium after homogenization at 1300° for 100 hours with subsequent quenching in water

Fig. 2. Microstructure of iron alloy containing 42% chromium after homogenization at a temperature of 1300° with subsequent quenching in water. 160 x

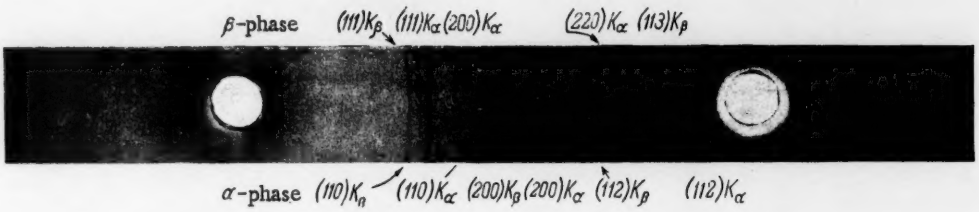

Fig. 3. Diffraction patterns of iron alloy containing 42% chromium after annealing at 1000°for 4 hours with subsequent quenching in water.

The Structure of the iron-vanadium alloys. After the sample of the alloy had been heated at the selected temperature and quenched in water, the microstructure was studied, and then powder for the x-ray investigation was filed from the surface of the sample. The powder was sealed in an evacuated capillary, and was again heated, with subsequent quenching, at the same temperature at which heating of the original sample had been carried out. The heating time was varied from 15 minutes to 2 hours at a temperature of 1400° and from 5 to 170 hours at 600°. The annealing was concluded when an increase in heating time did not produce a further change in the structure of the sample.

The diffraction patterns were made with chromium radiation. The results of the investigation showed that, after homogenization at 1300° and quenching, the alloys of iron with vanadium containing from 28.5 to 74% vanadium were not single-phase (as would be expected from the structural diagram of Wever and Lellinghaus), but were two-phase. During the microscopic investigation, it was observed that in the background of α-phase crystals with a hardness of ~250 kg/sq. mm were crystals of another phase with a hardness of ~750 kg/sq. mm. The amount of the second, harder phase increased with an increase in the vanadium content of the alloy. The x-ray data confirmed the data from the microscopic investigation. Two systems of lines appeared on the pattern; one of these corresponded to the cubic, body-centered α-phase, and the other corresponded to a face-centered phase, which we designated the β-phase. By using the method of homometric pairs, from the ratio of the intensities of the lines of the α- and β-phases it was determined that the content of β-phase was 5% in the alloy containing 28.5% V and ~80% in the alloy containing 74% V. The β-phase lattice constant for the Fe alloy with 43% V was 4.12 A. The lattice constant changed only by hundredths of an angstrom with a change in the vanadium content.

After the investigation of the structure at a temperature of 1300°, the same samples were annealed and quenched at temperatures of 1400, 1200, and 1150°; just as in the samples quenched from 1300°, the structures

of all Fe–V alloys proved to be made up of two phases – α and β. At a temperature of 1150°, the structure of the Fe alloys containing 28.5, 42, and 49.5% V remained two-phase with an increase in the annealing time to 60 hours.

A different picture appeared on annealing the Fe–V alloys at 800°. At this temperature, even after heating for 5 hours and quenching, the Fe alloys with 28.5% V consisted of a single α-phase, while the alloys with 43, 49.5, and 74% V consisted of two phases – α and σ. After annealing at a temperature of 600°, the alloy with 28.5% V retained the α-phase structure, the alloy with 43% V consisted of α- and β-phases, and the α-phase crystals disappeared from the alloy with 49.5% V, the structure consisting only of the σ-phase.

Consequently, in iron alloys with from 28.5 to 74% vanadium, with a decrease in temperature from 1400 to 600° the phase transitions proceed by a more complex route than is apparent from the structural diagrams available in the literature, i.e.: $(\alpha+\beta) \rightarrow \alpha \rightarrow (\alpha+\sigma) \rightarrow \sigma$.

When the alloys were heated in the reverse direction from 600 to 1300°, the α-phase was converted to α- and β-phases, which indicates that the β-phase is the equilibrium phase, and at temperatures above the σ- to α-phase transition, alloys of Fe with 28.5 to 74% V consist of α- or α + β-or of the β-phase.

The structure of the iron–chromium alloys. As with the Fe–V alloys, thermal treatment of the Fe–Cr alloys was carried out by homogenization at a temperature of 1300° with subsequent quenching in water. After the microscopic and x-ray investigations, the same samples were annealed and quenched at temperatures of 1400-900°. The microscopic and x-ray investigations showed that, after quenching from a temperature of 1300°, the structure of the Fe alloys containing 35, 42, and 48% Cr consisted of α- and β-phase crystals. The amount of β-phase decreased with a decrease in the temperature. Thus, the Fe alloy containing 42% Cr contained 100% β-phase at a temperature of 1400°, while the β-phase content was approximately 90% at 1300° (Figure 1). After quenching of this alloy from 1300°, the microstructure consisted of α-phase crystals in the background of the β-phase crystals (Figure 2). After annealing of the alloy at a temperature of 1000° for an hour, only 10% of the β-phase was retained in the alloy (Figure 3). When the annealing time was increased so that equilibrium was established at 1000°, the alloy consisted only of α-phase. The lattice constant of the Fe alloy containing 42% Cr was 3.65 A.

Consequently, in iron-chromium alloys containing 35-48% chromium, just as in iron vanadium alloys containing 28.5-74% vanadium, the phase transformations include not only a polymorphic transformation of σ- to α-phase, but also a transformation of the α-phase into a face-centered β-phase lattice.

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M. V. Lomonosov Moscow
State University

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ON THE QUASI-BINARY SYSTEM: SIX-COMPONENT NICKEL SOLID SOLUTION + TITANIUM CARBIDE

I. I. Kornilov, L. I. Priakhina, O. V. Ozhimkova and A. Ia. Snetkov

(Presented by Academician I. I. Cherniaev, October 11, 1957)

The absence of general principles guiding the study of multicomponent systems and the difficulties involved in their graphic representation require the development of new rational methods for their investigation.

The tendency of metals toward the formation of solid solutions, compounds, and solid solutions based on such compounds leads to the formation of considerably fewer phases in multicomponent systems than would be assumed from the number of participating components.

The presence of a chemical affinity between the elements and a definite degree of activity of the reacting elements in a multicomponent system permits reduction of the investigation of the latter to a study of the equilibrium among a limited number of phases (two-, three-, and four-phase equilibrium). Some questions of the theory of structural diagrams of multicomponent metallic systems have been considered in reference [1].

In this connection, in a number of cases the study of certain multicomponent systems can be reduced to an investigation of a three-phase equilibrium: multicomponent liquid solution $\rightleftarrows$ multicomponent solid solution + metallic compound.

As an example of this, we took the 8-component nickel system Ni–Cr–W–Mo–Nb–Ti–Al–C, in which, with a specific combination of components, a three-phase system can be obtained: 8-component liquid solution $\rightleftarrows$ 8-component solid solution + a compound of TiC or its solid solution.

TABLE 1

Heat of Formation of the Carbides

Carbides	Ni_3C	Fe_3C	Mo_2C	WC	TaC	Cr_4C	NbC	VC	TiC
Heat of formation—ΔH kcal/mole	−9.2	−5.8	−4.0	+8.4	+9.0	+16.0	+19.0	+28.0	+57.0

On the basis of the heats of formation of the carbides of nickel, chromium, tungsten, molybdenum, niobium, and titanium (see Table 1), it is possible to predict the course of the reactions in the 8-component nickel system containing the above-indicated elements, and it may be assumed that titanium carbide will be preferentially formed.

Titanium carbide is formed with the greatest evolution of heat, and is the most stable of all of the possible carbides in the system studied.

For confirmation of the proposals indicated above, we studied the chemical interaction of titanium carbide with a 6-component nickel solid solution (containing Cr, W, Mo, Nb, and Al), which was taken as the initial phase, and phase equilibrium was established in this 8-component system.

The composition of the initial 6-component nickel solid solution was chosen to be: Ni, 82%; Cr, 7%; W, 3%; Mo, 3%; Al, 3% and Nb, 2%.

Alloys consisting of the initial 6-component nickel solid solution to which was added titanium carbide in amounts of from 0 to 95% were prepared for the investigation.

The alloy samples were prepared by fusion in an induction furnace (up to 15% TiC) and by powder metallurgy (from 25% to 95% TiC).

Thermal, metallographic, x-ray, and intermetallide analytical methods were applied in the investigation. Moreover, the hardness of alloys enriched with nickel was studied after quenching from 1250, 1200, and 1000°.

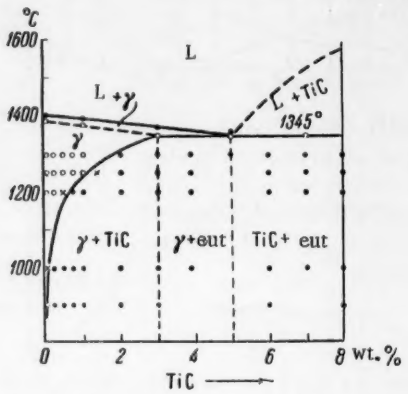

Fig. 1. Melting-point diagram of the system: 6-component nickel solid solution (γ_6) – titanium carbide (TiC). The crosses show the solubility limits according to data from the x-ray structural analysis.

Thermal analysis was used for the determination of the crystallization temperature interval of the alloys containing from 0 to 15% TiC. The cooling curves were recorded on an N. S. Kurnakov pyrometer using a platinum–platinum-rhodium thermocouple.

The melting-point diagram of the system 6-component nickel solid solution – titanium carbide is shown in Figure 1. In Figure 1, the 6-component nickel solid solution is denoted by γ_6. As can be seen from the diagram, the nickel solid solution γ_6 crystallizes with titanium carbide as an eutectic with limited solubility of the phases.* The liquidus line drops from the melting point of γ_6 at 1400° to the eutectic temperature of 1345°, where the mixture has a TiC content of 5%. Crystallization of the alloys investigated occurred within a narrow temperature interval (10-20°).

A microstructural investigation of the cast and quenched alloys confirmed the eutectic structure of the corresponding alloy compositions.

Quenching of alloys containing from 0 to 10% TiC was carried out at temperatures of 1300, 1250, 1200, and 1000° in order to determine the solubilities of TiC in the 6-component nickel solid solution. Soaking time at the indicated temperatures was 100 hours.

The determination of the solubilities was carried out by metallographic and x-ray methods.

According to the data obtained, the solubility of TiC in the 6-component nickel solid solution varies with temperature. At 1250°, the solubility of TiC is 1.4%, at 1200° it is 0.5%, and it is about 0.1% TiC at 1000°.

In alloys containing more than 5% TiC (hypereutectic), the phase first crystallizing is titanium carbide, coarse crystals of which (cubic form) were disseminated in the eutetic mixture.

In the alloy with 50% TiC, after quenching from 1300°, coarse crystals of TiC surrounded by the eutectic mixture were observed.

Selective solution of the solid solution γ_6 liberated only a single carbide phase from alloys containing 1.0, 4, and 7.5% TiC.

Preliminary chemical analysis of the liberated phase indicated the presence of niobium, molybdenum, tungsten, chromium, and aluminum, along with titanium and carbon. Obviously, these elements enter into the titanium carbide-containing solid solution. The composition of this phase varies with the composition of the initial alloy.

* Although the cooling curve of the alloy having the composition of the eutectic mixture indicated crystallization at almost constant temperature, the authors consider that here there can be no invariant equilibrium.

According to the x-ray data, this phase has a face-centered cubic lattice of the TiC type. The lattice parameter varies from 4.38 to 4.33 kX.

This change in the lattice parameter of the phase can be explained by a change in the composition of the phase, which depends on the ratios of the components of the original alloy. With an increase in the titanium carbide content, the percentage of titanium in this phase increases while retaining an atomic ratio of the metal (Ti, Nb, Mo, W, Cr, and Al) to carbon of 1:1.

This investigation demonstrates the possibility of studying multicomponent metallic systems by reducing them to an equilibrium among a limited number of phases.

The structural diagram of the quasi-binary system 6-component system nickel solid solution (γ_6) – titanium carbide (TiC) was constructed with the aid of the methods of thermal analysis and of metallographic and x-ray investigations. It showed the eutectic nature of the crystallization of the phases with mutually limited solid solutions of these phases.

The solubility of titanium carbide in the 6-component nickel solid solution was determined. At 1300°, it was 1.9% TiC. With a decrease in temperature, the solubility of TiC decreased and was 1.4, 0.55, and 0.15% TiC at temperatures of, respectively, 1250, 1200, and 1000°.

The presence of only two phases – γ_6-solid solution based on nickel and a phase based on titanium carbide – was established in the quasi-binary system studied.

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October 1, 1957

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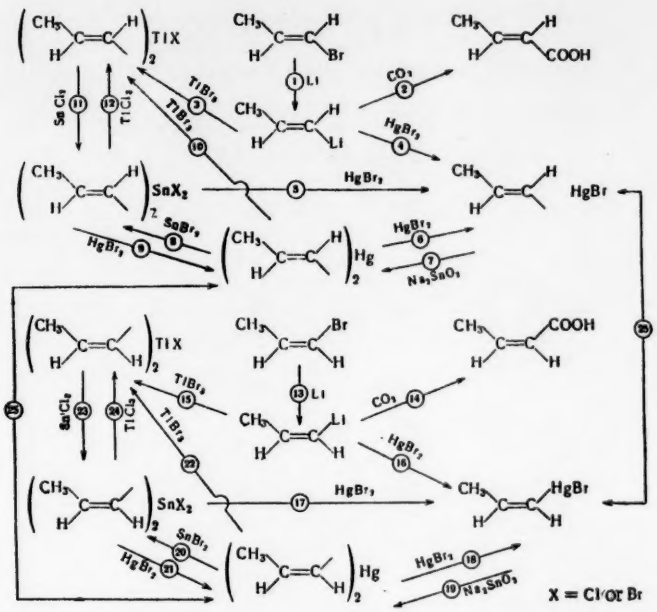
RETENTION OF CONFIGURATION BY A PROPENYL RADICAL DURING REACTIONS INVOLVING TRANSFER FROM METAL TO METAL

Academician A. A. Nesmeianov, A. E. Borisov and N. V. Novikova

Continuing our investigations [1] of the stereochemistry of reactions involving the exchange of atoms bound to an olefinic carbon, we carried out the series of reactions shown in Table 1, which reactions consisted of a series of transfers of a cis- or, correspondingly, trans-propenyl radical; the series started with the stereoisomeric 1-bromo-1-propenes. These bromides were converted by the action of lithium in ether at a temperature of from +5 to −7° into the corresponding stereoisomeric propenyllithiums and then, by a series of exchange reactions at reduced temperatures, into a series of organometallic propenyl compounds of Hg, Sn, and Tl and by the action of CO_2 into the corresponding stereoisomers of crotonic acid.



The configurations of the original bromopropenes [2] and also those of crotonic and isocrotonic acids are known. The configurations of both propenyllithiums, which were obtained by the action of lithium on an ether solution of the respective bromopropenes, were proved by the presence of bands at 700 and 1623 cm^{-1} in the infrared spectrum of the substance formed from cis-bromopropene and by the presence in the infrared spectrum of the stereoisomer of bands at 975 and 1645 cm^{-1},* which characterize the first organolithium compound as the cis- and the second as the trans-isomer.

* The infrared spectra of the propenyllithium stereoisomers were obtained at our request by L. A. Kazitsina and G. A. Rudenko, for which we tender out thanks.

The exchange reactions of both propenyllithium isomers with $HgBr_2$ and $TlBr_3$ proceeded with retention of configuration, as did all remaining exchanges of metals studied by us. This was shown by restriction of the field of transformations of cis-propenyllithium from the field of transformations of the trans-lithium compound and the method of even and odd cycles [1]. Actually, conversions 6, 7; 7, 8, 5; 7, 8, 12, 11, 5; 7, 8, 12, 11, 9, 6 and 11, 9, 10 in the series of transformations of trans-propenyllithium and the corresponding conversions 18, 19; 19, 20, 17; 19, 20, 24, 17; 23, 24; 23, 21, 22 include 2, 3, 5 and 6 steps, and they are cyclic; i.e., they return each time to the original stereoisomer regardless of the number of steps in the cycle. Therefore, in all probability, reactions with inversion of configuration are excluded.

Thus, the material presented in the present article (partly already reported in reference [3]) again confirm the rule, established by us, of the retention of configuration during electrophilic or homolytic substitutions at an olefinic carbon.

In the present work, conversions 1, 13, 8, 20, 11 and 23 are obviously homolytic, and the rest are electrolytic. All reactions were carried out at temperatures below room temperature. For this reason, we were not able to use reactions of the type $R_2TlX+Hg \rightarrow R_2Hg$, which we used earlier; they require a considerably higher temperature.

Institute of Heteroorganic Compounds
Academy of Sciences USSR

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EUROPIUM HEXABORIDE

G. V. Samsonov, V. P. Dzeganovskii and I. A. Semashko

(Presented by Academician I. I. Cherniaev, November 28, 1957)

The hexaborides of the rare earth metals, MeB_6, have now been rather well studied [1]. These compounds, as a result of their high thermoemissive nature, find use in electronics. One of the few as yet unsynthesized and uninvestigated hexaborides is europium hexaboride.

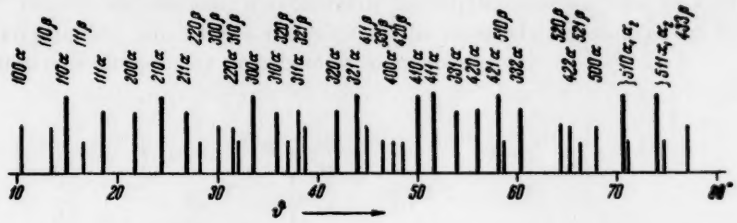

Fig. 1. Tracing of the diffraction pattern of EuB_6

In the present work, this compound was obtained by reaction of pure europium oxide with boron carbide:

$$Eu_2O_3 + 3B_4C = 2EuB_6 + 3CO.$$

TABLE 1

X-ray Data for Europium Hexaboride

hkl	ϑ	I_{exp}	*hkl*	ϑ	I_{exp}
100	10° 33′	av.	400	47° 39′	w.
110	15° 00′	v. s.	410	49° 54′	v. s.
111	18° 33′	s.	411	51° 39′	v. s.
200	21° 45′	s.	331	53° 45′	s.
210	24° 21′	v. s.	420	56° 03′	s.
211	26° 48′	s.	421	58° 09′	v. s.
220	31° 30′	av.	332	60° 18′	s.
300	33° 39′	v. s.	422	65° 15′	av.
310	35° 48′	s.	500	67° 51′	av.
311	37° 57′	s.	$510\alpha_1$	70° 39′	v. s.
320	41° 57′	s.	$510\alpha_2$	71° 06′	w.
321	43° 51′	v. s.	$511\alpha_1$	73° 57′	v. s.
			$511\alpha_2$	74° 24′	w.

The reaction was carried out under vacuum at 1650° for 2 hours. The product— a dark gray powder — corresponded precisely to the formula EuB_6, and had a carbon content of less than 0.02%. The x-ray structural investigation, which was carried out by the powder method using copper radiation and an RKD-type camera with a diameter of 57.3mm, showedthat europium hexaboride has a cubic lattice with an identity period of

$a = 4.167 \pm 0.002$ A (space group O_h^1, which is characteristic of all hexaborides of the rare earth metals). A tracing of the powder pattern is shown in Figure 1, and the corresponding numerical data are presented in Table 1. The density calculated from the lattice period is 4.99 ± 0.01 g/cc.

This value of the lattice period of europium hexaboride confirms the hypothesis [2] of the correspondence between curves showing the change in atomic radii of the rare earth metals and those showing the change in lattice period of these metals, and it also confirms the conclusion, based on this conformity, as to the effective positive trivalence of all rare earth elements in their compounds, with the exception of europium and ytterbium, which displays a divalent character, noted as sharp maxima on the curves of the atomic radii of the metals and on the curves of the lattice periods of their hexaborides (Figure 2).

In addition to the value for EuB_6, values previously obtained by us for the lattice periods of DyB_6, HoB_6, and LuB_6 [3] were used for the construction of the lattice period curve. The curve permits a choice to be made between the available values of the lattice period of GdB_6, $a = 4.112-4.110$ A [2, 4] and $a = 4.13-4.14$ A (the latter is the more correct value on this basis), and it also permits estimation, by interpolation, of the as yet undetermined values of the lattice periods of prometheum hexaboride ($a \cong 4.128$ A), terbium hexaboride ($a \cong 4.12$ A), and thullium hexaboride ($a \cong 4.11$ A). It is probable that the value reported by Kiessling [5] for the lattice period of erbium hexaboride is too low.

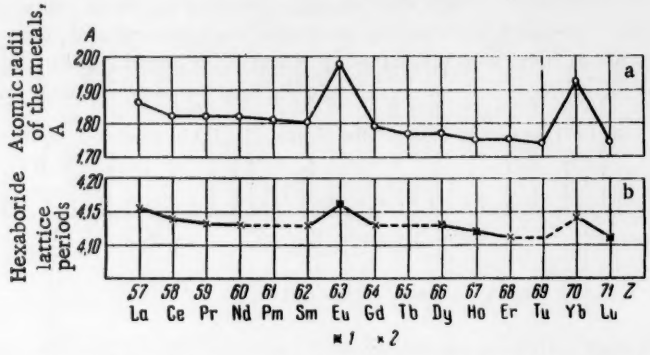

Fig. 2. a – atomic radii of the rare earth metals from the data of reference [8], b – lattice periods of their hexaborides. 1 – our data, 2 – data of other authors.

It should be noted that the regularity pointed out above places under doubt the evaluation in reference [7] of the lattice period of ytterbium hexaboride as requiring correction. On the contrary, this value, just as the value of the lattice period of EuB_6, strictly conforms to the regularity with which the rare earth metals retain their effective valence in their compounds.

Institute of Metal-Ceramics and Special Alloys
Academy of Science USSR

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•Original Russian pagination. See C.B. Translation.

MERCURATION OF POLYSTYRENE

R. N. Smirnov

(Presented by Academician A. V. Topchiev, November 27, 1957).

Until recently, chemists working in he field of high-molecular-weight materials have confined themselves to the synthesis of new monomeric compounds. The polymeric material resulting from such syntheses has rarely been considered as raw material for further synthesis. However, the point of view on this question has recently changed, and a large amount of work devoted to so-called "graft polymers" has appeared.

The present work was devoted to the synthesis of new polystyrene derivatives obtained by means of organomercury compounds. Mercuration has long been used for the analysis of polymers; however, no attention has been given to the study of the mercury derivatives, and these derivatives have not been used for synthesis.

The mercuration of polystyrene naturally proceeds under conditions other than those given by Nesmeianov and Freidlina [1, 2] for the reaction with the monomer and other than those given by Markarova and Nesmeianov [3] for the reaction with alkylaromatic compounds.

A polystyrene, from the Kuskov Chemical Plant, $N_{cp} \approx 1000$ (inspection data), was selected for the work. The material was purified by two-fold reprecipitation from benzene solution and washing with a mixture of methyl alcohol and benzene (3:1); it was then ground and dried at 105°. Mercuration of the polystyrene with mercuric acetate in water and in methyl and ethyl alcohol proceeded very poorly. Only 17-18% substitution could be obtained by reaction in boiling solvent for 25 hours.

Mercuration in acetic acid proceeded in an unusual manner. At temperatures up to 50°, sorption of the mercuric acetate was the main reaction; in boiling acid, the polystyrene partially charred, and, in addition, a brown, light, amorphous product and metallic mercury were formed. The best preliminary swelling of the polystyrene in a solution of mercuric acetate in acetic acid was obtained with the following proportions: 10 g polystyrene, 200 ml of glacial acetic acid, and 30 g of mercuric acetate. After a lapse of 4-5 days, the reaction mixture was transferred to a three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer, and the reaction was carried out over a period of 10 hours while gradually raising the temperature from 50 to 100° until the product dissolved. After solution of the polymer, the stirrer speed was increased to 100-120 rpm, and the mixture was brought to boiling.

After the solution stage, the precipitation stage set in; the reaction was usually stopped soon after this, since scorching of the product in the bottom of the flask began. The hot solution was poured, with stirring, into cold water, and the precipitate was washed with hot water by decantation. The brittle precipitate was ground in a mortar, and again washed with hot water. The presence of Hg ions in the product was readily detected by means of the color reaction with KI. To remove the Hg ion, the mercury derivative was swelled in acetic acid for 20-30 hours, and 10-15 ml of perhydrol was then added to it; oxidation was allowed to proceed for 30 minutes, and the solution was then decanted and treated with water as described previously.

The mercury derivative of polystyrene is a white, brittle material which is insoluble in the usual organic solvents but which swells considerably in glacial acetic acid and mixtures of it with benzene and acetaldehyde and in pyridine and quinoline.

In Table 1 are presented analytical data on the original polystyrene and two of its mercury acetate

TABLE 1

Results of Elemental Analyses of Polystyrene and Its Derivatives

	C, %	H, %	N, %	S, %	Hg, %	O, % (by difference)	Substitution in the benzene rings	
							in % of polystyrene	in % of mercury derivative II
Polystyrene	92.30	7.70						
Mercury acetate derivative I					34.17		62.12	
Mercury acetate derivative II					28.34		51.71	
Copolymer of styrene with phenyl p-vinylphenyl sulfone	81.72	7.85	—	4.56	—	5.87	34.8	67.1
Copolymer of styrene with p-nitrophenyl p-vinylphenyl ketone	80.10	6.14	2.17	—	—	11.59	28.5	55.1
Copolymer of styrene with p-vinylacetophenone	88.56	7.55	—	—	—	3.89	31.1	59.9
Copolymer of styrene with p-vinylphenylacetic acid	82.36	7.00	—	—	—	10.64	45.4	87.8

derivatives. From mercury acetate derivative II, pre-swollen in glacial acetic acid, were synthesized copolymers corresponding to the following reactants: benzenesulfonyl chloride, p-nitrobenzoyl chloride, bromoacetic acid, and acetyl chloride. The syntheses were carried out in the previously described apparatus using a reactant ratio of 1:1.5; the reactants were first heated for 10 hours on a water bath and then for 4-6 hours in boiling acetic acid. After the reaction was complete, 5-10 ml of perhydrol was added to oxidize the Hg ion; the contents of the flask were then diluted with water, and the precipitate was washed on the filter with water, then with 5% HCl, and again with water.

Fig. 1. Thermal decomposition of polystyrene mercury acetate derivative I (by the method of N. S. Kurnakov).

The reaction products were dissolved in organic solvents, filtered from metallic mercury, and washed with aqueous solutions of $NaHCO_3$ and with water. The copolymers were recovered by precipitation by dilution. It should be noted that with the small amounts of the mercury acetate derivative of polystyrene used in the reactions, low yields of the copolymers were obtained owing to their heterogeneity and to the high losses during purification of the samples.

Analyses of these samples, which are nominally called copolymers, were substantially different from the theoretically calculated analyses.

Thus, the substitution reaction of a mercury acetate group in polystyrene proceeds in an unusual manner, and leads both to reduction products and to substitution products. The lack of stoichiometric ratios of N to O and of S to O obviously shows that the acetic acid participates in the reaction. Similar results were obtained more rapidly (15-25 minutes) in pyridine medium, but the pyridine did not enter into the reaction; this may be seen from the analytical results. A comparison of the results of the reaction with the polymer and with the styrene monomer shows that with the polymer, the reaction proceeds in a more complex manner. The explanation of this fact probably must be sought in the little-studied stereochemistry of macromolecules.

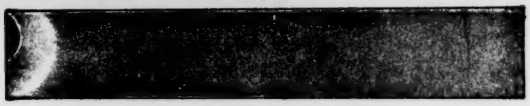

Fig. 2. x-Ray pattern of polystyrene (filtered copper radiation).

Fig. 3. x-Ray pattern of polystyrene mercury acetate II (filtered copper radiation, 40-hour exposure).

In Figure 1 is shown the thermogram for the decomposition of polystyrene mercury acetate derivative (Sample I) by the method of N. S. Kurnakov; this curve shows the comparatively low thermal stability of the substance. From the thermogram, it can be concluded that the mercury acetate derivative of polystyrene can hardly find use as a plastic; however, numerous possibilities exist for the synthesis of new high-molecular-weight substances from the mercury derivative.

According to x-ray data, polystyrene (Figure 2) and its copolymers are amorphous substances, but the mercury acetate derivative (Figure 3) is crystalline. Thus, mercuration can be used for structural analysis of certain high-molecular-weight substances.

The x-ray analyses were carried out by B. V. Lukinyi and the elemental analyses were by A. A. Zakharova. The author is happy to acknowledge their assistance in this work.

Institute of Fossil Fuels Academy of Sciences USSR Received Novermber 26, 1957

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*Russian translation.

POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF BORON TRIFLUORIDE ON ACTIVATED CARBON

Academician A. V. Topchiev and L. A. Aliavdina

The authors of the first paper on the catalytic action of boron trifluoride during the polymerization of olefins, A. M. Butlerov and V. Goriainov [1], reported that propylene polymerizes under the influence of boron trifluoride.

In the present work, the effect of temperature, space rate, carrier, and catalyst-contact time on product distribution and conversion during the polymerization of isobutylene in the presence of boron trifluoride was studied. The polymerization was carried out in the gas phase and at atmospheric pressure.

In addition, we studied the conditions for the use of and the cause of the catalytic action of the new molecular compound $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ [2] in the polymerization of isobutylene [3], which has not been investigated up to the present.

The isobutylene, which contained 97-98% unsaturates, was prepared by the catalytic dehydration of isobutyl alcohol (b. p. 107°) at 400° over aluminum oxide. The boron trifluoride was prepared by heating 1 part by weight of B_2O_3, 2 parts by weight of CaF_2, and 10 parts by weight of 5% oleum. The boron trifluoride was freed from water vapor and hydrogen fluoride by passing it through a flask filled with sulfuric acid containing boric oxide.

The activated carbon was dehydrated under vacuum at 300°. 100 cc, or 20 g, of the dry activated carbon was then placed in a tube, and the latter was inserted in an electric furnace. Dry boron trifluoride was passed through the tube at 150°, and the amount adsorbed by the activated carbon was determined from the weight increase. The carbon samples were brought to constant weight, which showed that adsorption of boron trifluoride was complete. Under the conditions indicated, 20 g of activated carbon adsorbed 4-5 g of boron trifluoride.

The resulting catalyst – boron trifluoride on activated carbon – was charged into the reactor, which was 40 cm long and 2.6 cm in diameter. The reactor was provided with a thermowell and an electric heater. The lower part of the reactor was connected to a tube 12 cm long and 2 cm in diameter, which was packed with small pieces of solid NaOH on glass wool to remove boron trifluoride. A calcium chloride tube was at the end of the system.

Polymerization of the isobutylene was carried out at 20, 70, 100, and 150° and rates of 6, 12, 18, and 30 liters/hour or space rates of 60, 120, 180, and 300 $hours^{-1}$, respectively. 50 liters of isobutylene was used for each experiment. In experiments at 20°, the reactor jacket was cooled with water.

As seen from Figure 1, I, at a space rate of 60 $hours^{-1}$, with an increase in temperature the amount of 99-126° fraction in the polymer increased to 33% and the amount boiling above 185° decreased to 12%. The isobutylene conversion was almost constant, varying from 98 to 99%. It is seen from Figure 1, II that at a space rate of 300 $hours^{-1}$, the isobutylene conversion decreased to 50% with an increase in temperature, while the content of residue boiling above 185° dropped to 7.5% and the amount of the 98-126° fraction increased to 48%.

In Figure 2 is shown the variation of d_4^{20} and n_D^{20} with temperature at space rates of 60 and 300^{-1}. In both cases, a decrease in density and refractive index of the polymer with an increase in temperature was noted.

At the same temperature, these values were less at a space rate of 300 hours^{-1}. Thus, our experiments showed that an increase in temperature and also an increase in space rate, or a decrease in contact time, reduced isobutylene polymerization. The physicochemical properties of polymers prepared at 150° and the properties of certain fractions of the polymers are given in Table 1.

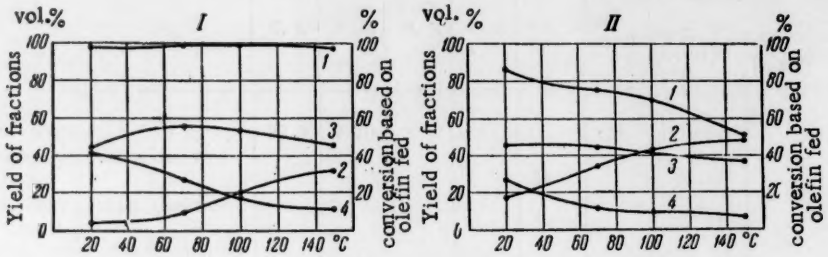

Fig. 1. Effect of temperature on isobutylene conversion (1) and on the yield of fractions of the polymer at space rates of 60 hours^{-1} (I) and 300 hours^{-1} (II) in the presence of BF_3 on activated carbon. 2 — 99-126° fraction (I) and 98-126° fraction (II); 3 — 170-185° fraction; 4 —185° fraction.

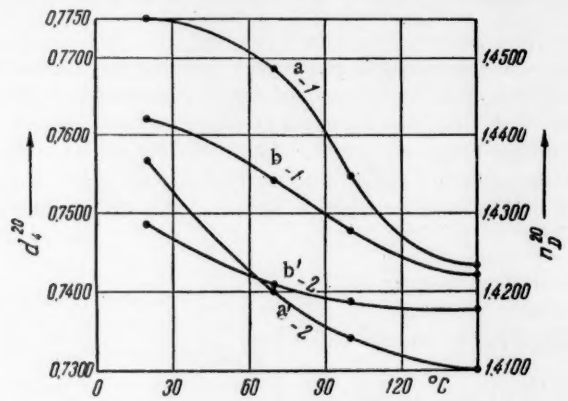

Fig. 2. Variation d_4^{20} (a) and n_D^{20} (b) of isobutylene polymer with temperature at space rates of 60 hours^{-1} (1) and 300 hours^{-1} (2) in the presence of BF_3 on activated carbon.

The K_2SO_4 and Na_2SO_4 used in the preparation of $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ were given a preliminary calcination. Then, in the apparatus used for the adsorption of boron trifluoride by carbon but at a temperature of 235° for K_2SO_4 and 330° for Na_2SO_4, the addition of boron trifluoride was carried out to form the molecular compounds, which were solid, crystalline materials. The samples were brought to constant weight, which showed that the addition reaction was complete.

After numerous experiments, it was established that the catalytic action of the molecular compounds $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ is due to boron trifluoride; these compounds were used in experiments on isobutylene polymerization with boron trifluoride in the feed gas, which were carried out at 150°.

20 g, or 100 cc, of dry activated carbon, which was placed in the reactor, was used for each experiment. Then, isobutylene in an amount of 50 or 100 liters and at a space rate of 60 hours^{-1}, and boron trifluoride from the molecular compound, which was heated in an electric furnace, were fed into the reactor. Decomposition of the molecular compounds was carried out with a gradual increase in the temperature from 360 to 390°. 17.8 g of $K_2SO_4 \cdot BF_3$ or 15.4 g of $Na_2SO_4 \cdot BF_3$, containing 5 g of boron trifluoride, was used for an experiment.

The resulting polymer was washed, dried, and distilled in a column. The results are presented in Table 1. The present experiments are the first to demonstrate the possibility of using the new molecular compounds $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ in the polymerization of isobutylene and to explain the nature of their catalytic action [3]. Decomposition of the molecular compound proceeds at an elevated temperature:

$$K_2SO_4 \cdot BF_3 \rightleftarrows K_2SO_4 + BF_3.$$

The liberated boron trifluoride is the catalyst for the reaction.

TABLE 1

Physicochemical Properties of the Polymers and Some of Their Fractions

Fraction, °C	Yield of fractions, vol.%	Isobutylene conversion, %	d_4^{20}	n_D^{20}	Bromine number	Unsat. hydrocarbons, %	Molecular weight	Space rate, hours^{-1}	Octane no.
Without BF_3 in feed gas									
98–106°	27		0.7195	1.4118	141	99.0	112.4	60	
170–185°	46		0.7613	1.4329	93	98.7	169.9	60	
Polymer		98	0.7432	1.4222	106	98.8	149.2	60	
Polymer		50	0.7309	1.4180			131.5	300	91
With BF_3 in feed gas									
98–106°	34		0.7168	1.4101	140	99.5	113.8	60	
170–185°	41.2		0.7602	1.4327	94	99.2	168.9	60	
Polymer		81	0.7357	1.4210	120	99.0	132.0	60	
Polymer		70	0.7277	1.4180				60	

An experimental method was also developed for using the molecular compound $K_2SO_4 \cdot BF_3$ with boron trifluoride in the feed gas, and it was shown that it is possible to obtain by this method lighter polymer than is obtained without BF_3 feed, as seen from Table 1.

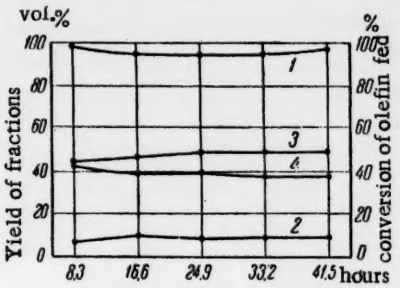

Fig. 3. Isobutylene conversion (1) and yield of polymer fractions as functions of the time on the catalyst; catalyst, BF_3 on activated carbon; temperature, 20°; space rate, 60 hours^{-1}. 2 – 100-126° fraction, 3 – 170-185° fraction, 4 – 185° fraction.

The catalyst life of a catalyst consisting of 5 g of BF_3 on 20 g of activated carbon was studied at 20°. 250 liters of isobutylene was used for the experiment, and it was fed at a space rate of 60 hours^{-1}. The results, which are presented in Figure 3, show that high isobutylene conversion was obtained over the entire length of the run, and consequently, a catalyst life considerably in excess of 41.5 hours is possible.

At an average conversion of 96%, 540 g of polymer was obtained from 250 liters of isobutylene. The physical constants of the polymer were: d_4^{20} 0.7715, n_D^{20} 1.4402, molecular weight 177.4, and octane number 87. The molecular weight was determined cryoscopically, and the octane number was determined by the motor method using a "Vokesh" apparatus.

Raman analyses were carried out on certain fractions of the polymer. The results are presented in Table 2.

The presence in the 108-120° fraction of 3,4,4-trimethyl-2-pentene, 2,3,4-trimethyl-2-pentene, and 2,3,4-trimethyl-1-pentene indicates that isobutylene polymerization was accompanied by isomerization; this was especially noticeable in the polymer obtained at 150° (7-9%).

In order to study the effect of the carrier on the polymerization of isobutylene in the presence of boron trifluoride, experiments with and without a carrier were carried out in parallel. In the latter case, activated carbon was not charged to the reactor, and only isobutylene and boron trifluoride from 17.8 g of $K_2SO_4 \cdot BF_3$ were fed, the former at a rate of 6 liters/hour. The temperature of the experiment was 150°, and the total amount of isobutylene was 50 liters.

TABLE 2

Spectral Analysis of Certain Polymer Fractions (catalyst – BF_3 on activated carbon)

Experiment temperature, °C	Space rate, hours^{-1}	Fraction, °C	Chemical composition	B. p., lit. value [4], °C
20	60	98–106	2,4,4-Trimethyl-1-pentene	101.36
			2,4,4-Trimethyl-2-pentene	104.85
150	60	98–106	2,4,4-Trimethyl-1-pentene	101.36
			2,4,4-Trimethyl-2-pentene	104.85
150	60	108–120	3,4,4-Trimethyl-2-pentene	112.3
			2,3,4-Trimethyl-2-pentene	116.26
			2,3,4-Trimethyl-1-pentene	117.15

The investigation showed that the isobutylene conversion was decreased by the absence of a carrier, and it was only 18.7% at the end of the experiment. In the experiment with a carrier, the conversion gradually increased to 96%. The average conversion was 43% in the first case and 81% in the second. These data indicate that it is expedient to use an activated carbon carrier in the polymerization of isobutylene with boron trifluoride.

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ON THE COMPOSITION OF THE ALCOHOLS OBTAINED BY LIQUID-PHASE OXIDATION OF n-PARAFFINIC HYDROCARBONS

A. N. Bashkirov, V. V. Kamzolkin, K. M. Sokova and T. P. Andreeva

(Presented by Academician A. V. Topchiev, December 14, 1957)

Investigations in the field of liquid-phase oxidation of paraffinic hydrocarbons previously led us to the development of a process directed toward the production of higher aliphatic alcohols [1, 2]. Direction of this process toward the production of alcohols was due to the presence in the reaction zone of boric acid and to the reaction conditions selected.

The study of the chemical composition and structure of the alcohols obtained in this process is of considerable interest in clarifying the mechanism by which the alcohols are formed and also in connection with the selection of methods for their efficient utilization. In previous investigations [3], it was established that secondary alcohols having the same carbon skeleton and number of carbon atoms per molecule as the original hydrocarbon are the major product of the liquid-phase oxidation of normal paraffinic hydrocarbons with a nitrogen-oxygen mixture containing 3.0-4.5% O_2 at a temperature of 165-170°, and in the presence of boric acid. The aim of the present investigation was the determination of the position of the hydroxyl group in the alcohol molecules.

In considering this problem, our attention was attracted by one of the chemical methods for investigating structures of organic compounds – the method of oxidation of alcohols by potassium dichromate in a dilute sulfuric acid medium [4].

Carboxylic acids with the same number of carbon atoms as the original alcohol are formed when primary alcohols are oxidized with this reagent. When secondary alcohols are oxidized, rupture of carbon-carbon bonds occurs at the site of the hydroxyl group, resulting in the formation of carboxylic acids with fewer carbon atoms per molecule. Consequently, from the composition of the acids obtained by oxidation of alcohols with this reagent it is possible to determine the position of the hydroxyl group in the alcohols investigated. However, the literature indicates that the reaction does not proceed entirely smoothly, and, in addition to acids formed by oxidation at the site of the hydroxyl group, acids of different molecular weight are also formed. Moreover, when the reaction is carried out in sulfuric acid at an elevated temperature, certain side reactions, leading to the formation of tar, also occur. Unfortunately, the literature is rather obscure on the question of the quantitative relationship between the main direction of the oxidation and the above-indicated side reactions.

In order to answer the question of whether it is possible to use this method for the determination of the position of the hydroxyl group in the alcohols under study, we studied the oxidation of individual aliphatic alcohols having their hydroxyl group in different positions (4-tetradecanol and 7-hexadecanol), identifying the acids and determining their yields. Oxidation of the alcohols was carried out by the method described by Krafft [4] for the preparation of undecanoic acid, though with some slight modifications. The weight ratio of alcohol to potassium bichromate was 1 : 3. The dilute sulfuric acid (about 50 weight % concentration) was taken in a ten-fold amount with respect to the alcohol. In order to avoid deep conversion, which leads to the formation of by-products, the oxidation was carried out initially at low temperature (cooling with ice), then at room temperature, and finally by heating on a boiling water bath. The acidic reaction products were isolated from the resulting oxidate through their sodium salts. These acids were converted to the methyl esters,

which were afterwards distilled in a fractionating column in the presence of an entrainer [5]. A mixture of hydrocarbons, freed from olefins and aromatics, was used as the entrainer. The ester numbers of the resulting fractions were determined, and from these the ester contents of the fractions were calculated. From the boiling ranges of methyl esters of acids of specific composition, it was possible to determine the distribution of the acids formed during the oxidation of the alcohols. The acids were recovered from the methyl esters, and were identified by means of their silver salts.

The resulting data permitted us to establish the presence of specific methyl esters in the individual fractions. Moreover, from the determinations of the silver content of the silver salts of the recovered acids, it also was possible to carry out calculations of the distribution of the acids. The calculations were carried out by means of a formula developed for the case of not more than two acids in a fraction:

$$x = \frac{A(M-1) - 107.9(100-A)}{14A} \cdot 100,$$

where $\underline{x}$ is the content of the acid C_n (in mole %), A is the silver content found for the silver salt (wt. %), and M is the molecular weight of the acid C_{n+1}.

The investigation in which certain representatives of higher aliphatic alcohols of the aliphatic series were used to study the oxidation of alcohols with potassium dichromate in dilute sulfuric acid showed that, under the conditions used, theyield of products was about 80% of the alcohol taken. The yield of acids was 75% of the reaction products, while the remaining 25% comprised neutral compounds (mainly ketones).

The investigation of the composition of the acids established that oxidation of the alcohols proceeded chiefly (90%) at the site of the hydroxyl group. Appreciable deviation from Popov's rule was observed as the hydroxyl group was moved away from the end carbon atom.

On the basis of these experimental data, it was felt that oxidation of alcohols with potassium dichromate in sulfuric acid with subsequent isolation and identification of the resulting acids could be used to establish the locations of the hydroxyl group in alcohols.

This method was applied by us to the determination of the locations of the hydroxyl group in alcohols obtained by the oxidation of n-hexadecane. The oxidation conditions and the method of isolation of the alcohols have been described previously [3]. The main alcohol fraction, which comprised about 85% of the total amount of monohydric alcohols isolated, was subjected to investigation. This alcohol fraction was oxidized by the method described above. A certain amount of neutral oxygen-containing compounds (ketones) was obtained as a result of the oxidation, and these compounds were again oxidized. The total yield of acids comprised 96% of the reaction products. Distillation of the methyl esters of these acids made possible the separation and identification of the following monocarboxylic acids: valeric, caproic, enanthic, caprylic, pelargonic, capric, hendecanoic, lauric, tridecanoic, and myristic. These acids were found to be present in approximately equimolar amounts (Table 1). Palmitic acid was not detected.

TABLE 1

Distribution of Acids Obtained from Hexadecanols (Products of the Oxidation of n-Undecane)

Acid	By boiling point of the methyl esters		By content of silver in silver salts	
	mmole	%	mmole	%
Valeric ($C_5H_{10}O_2$)	3.52	8.0	3.29	7.5
Caproic ($C_6H_{12}O_2$)	3.73	8.5	4.10	9.3
Enanthic ($C_7H_{14}O_2$)	5.11	11.5	5.02	11.3
Caprylic ($C_8H_{16}O_2$)	4.18	9.5	3.95	9.1
Pelargonic($C_9H_{18}O_2$)	4.52	10.2	4.52	10.2
Capric ($C_{10}H_{20}O_2$)	4.49	10.2	5.42	12.2
Hendecanoic($C_{11}H_{22}O_2$)	4.52	10.3	4.20	9.5
Lauric ($C_{12}H_{24}O_2$)	4.17	9.5	4.50	10.2
Tridecanoic ($C_{13}H_{26}O_2$)	4.16	9.4	5.20	11.8
Myristic ($C_{14}H_{28}O_2$)	4.83	10.9	3.90	8.9
Palmitic ($C_{15}H_{30}O_2$)	0.87	2.0	—	—

These results lead to the conclusion that the alcohol fraction investigated was a mixture of secondary n-hexadecyl alcohols. The possible isomeric alcohols are present in this fraction in approximately equimolar amounts.

Thus, it was established that oxidation of n-paraffinic hydrocarbons in the liquid phase (in the presence of boric acid) yields primarily secondary alcohols comprising a mixture of all possible isomers. No appreciable difference was observed in the reactivity toward oxygen of the second, third, fourth, etc. carbon atoms in the molecules of higher paraffinic hydrocarbons of normal structure. This provides a basis for proposing that, under the oxidation conditions used, the reactivities toward oxygen of the secondary carbon atoms in the molecules of higher n-paraffinic hydrocarbons are practically equal; this provides for the formation during oxidation of hydrocarbons of all possible isomers of secondary alcohols.

Institute of Petroleum Academy of Sciences USSR

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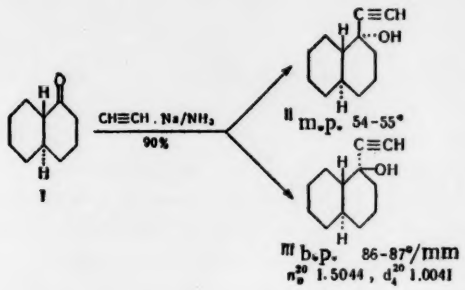
SYNTHESIS AND TRANSFORMATIONS OF CIS- AND TRANS-1-ETHYNYL-1-DECALOLS

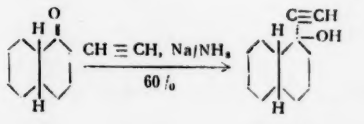
Academician I. N. Nazarov,* G. V. Aleksandrova and A. A. Arkhem

We have studied the condensation of cis- and trans-α-decalones with acetylene with the aim of using the resulting acetylenic alcohols for the synthesis, by methods developed in our laboratory [1], of decalins with dihydroxyacetone, glycerin, and dihydroxycarboxylic groups, which are characteristic of corticoid hormones.

The condensation of trans-α-decalone with acetylene was carried out under pressure in the presence of powdered potassium hydroxide [2] and also in solution in liquid ammonia in the presence of sodium [3]. In the latter case, a mixture of the isomeric trans-1-ethynyl-1-decalols was obtained, from which the epimeric trans-1-ethynyl-1-decalols II and III were isolated by freezing at – 70° and chromatographing over aluminum oxide: the ratio of II and III was 1 : 2. [Yields, in per cent, are indicated under the arrow; physical constants (m. p., b. p., n_D^{20}, d_4^{20}) of the compounds obtained are shown under the formulas.]

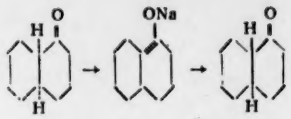


As is well known, cis-α-decalone readily isomerizes into trans-α-decalone under the influence of acids and alkalies [4, 5]; therefore, it appeared unlikely that cis-1-ethynyl-1-decalols would be obtained under the strongly alkaline conditions of the Favorskii method of acetylene synthesis. However, when cis-α-decalone IV was reacted with sodium acetylide in solution in liquid ammonia, cis-1-ethynyl-1-decalol V was obtained in an overall yield of 60%.



During this reaction, only about 10% of the cis-α-decalone IV underwent isomerization and was isolated as trans-α-decalone I. It appears that the condensation with acetylene successfully competed with the isomerization reaction, which proceeds through an enolization stage:

* Deceased.



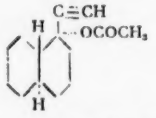
IV I

That trans-α-decalone, and not trans-acetylenic alcohols, was isolated from the reaction mixture excludes an enol mechanism for the acetylene synthesis and again confirms the correctness of the organometallic mechanism of this reaction [2]. The sterically selective course of the acetylene synthesis, with the formation of only the single cis-1-ethynyl-1-decalol V, is in agreement with the previously described reactions of addition to the carbonyl group of cis-α-decalone [6].

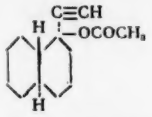
At the present time, it is universally considered that the conformation of cis- and trans-decalin is determined by the combination of the two cyclohexane rings in the chair form [7] in which there are two geometrically unequivalent types of bonds between the carbon atoms and the substituents occupying an equatorial (e) or axial (a) position [8].

It is known from the literature that esterification of compounds with axially located hydroxyl groups and hydrolysis of the corresponding esters are sterically more difficult than addition reactions with equatorially located hydroxy groups. Acid phthalates obtained from trans-α- and trans-β-decalols with equatorially located alcoholic groups saponify 19 and 7 times, respectively, more rapidly than esters of the epimeric decalols with axially oriented hydroxyl groups.

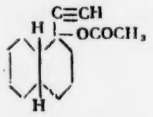
Acetylation of 1-ethynyl-1-decalols II, III, and V with acetic anhydride [11] gave high yields of the corresponding acetates VI, VII, and VIII,



VI b.p. 106—108°/2 mm n_D^{20} 1.4940. d_4^{20} 1.0344

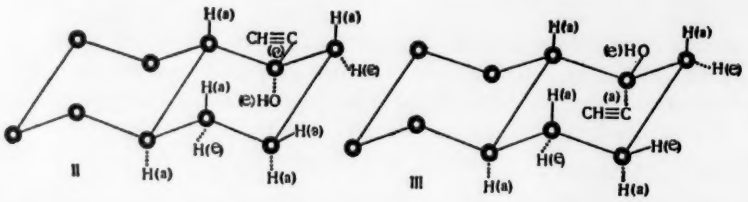


VII m.p. 79—80°

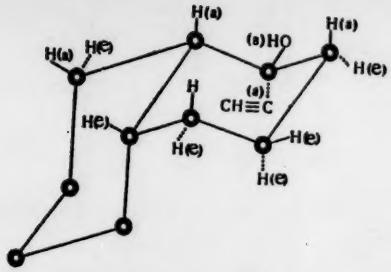


VIII m.p. 65—67°

and it was further observed that acetylenic alcohol III and its derivatives form acetyl derivatives more readily than the epimeric alcohol II. By analogy to trans-α-decalol, it can be assumed that the hydroxyl group in alcohol III is in an equatorial position, while it is axial in the more difficultly acetylated isomer II.

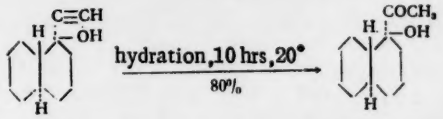


From cis-1-ethynyl-1-decalol V and its derivatives, it was very easy to prepare the acetates. Considering the overall asymmetry of the cis-decalin molecule, it can be assumed that one of the isomers of the cis-acetylenic alcohols (with axial hydroxyl) should esterify with extreme difficulty. Therefore, the ease with which alcohol V and its derivatives form acetates indicates, in all probability, an equatorial position of the hydroxyl group in these compounds.

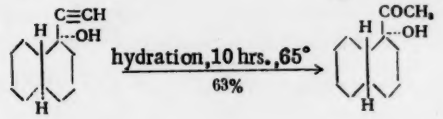


When comparative experiments were carried out on the rates of hydration of acetylenic alcohols II, III, and V in aqueous methanol in the presence of mercuric sulfate, it developed that trans-1-ethynyl-1-decalol III was hydrated completely in 10 hours at 20°, forming trans-1-acetyl-1-decalol IX.

The hydration of acetylenic alcohol II was accomplished under the same conditions but with a 10-hour refluxing at 65°, trans-1-acetyl-1-decalol X being formed. At 20°, acetylenic alcohol II did not undergo hydration, and was recovered completely unchanged. The isomeric acetates VI and VII behave similarly during hydration.



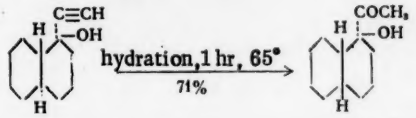
III IX B.p. 80—82°/1 mm
n_D^{20} 1.4898. d_4^{20} 1.0337



II X B.p. 106—107°/2 mm
n_D^{20} 1.4970. d_4^{20} 1.0502

Trans-1-acetyl-1-decalol IX readily formed both a semicarbazone and a 2,4-dinitrophenylhydrazone, while only a semicarbazone was obtained with great difficulty from trans-1-acetyl-1-decalol X, which is evidence of shielding of the acetyl group in this compound.

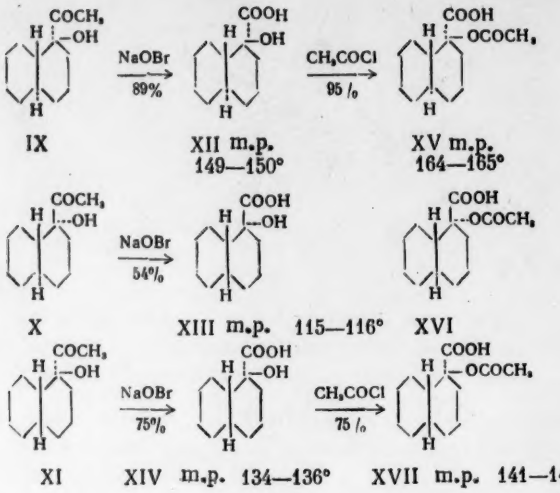
Hydration of cis-1-ethynyl-1-decalol also did not go at 20°; however, refluxing one hour at 65° turned out to be sufficient for the preparation of cis-1-acetyl-1-decalol XI, which gives only a semicarbazone, and that with difficulty, and does not form a 2,4-dinitrophenylhydrazone.



V XI M.p. 36—37°

These data are evidence that the carbon chain in compounds V and XI are also appreciably shielded by the neighboring cyclohexane ring. A sharp distinction in the rates of hydration of 9-methyl-1-ethynyl-6-oxodecalols having opposite configurations of substituents at C_1 has also been noted previously [12].

Oxidation with sodium hypobromite of acetyldecalols IX, X, and XI gave the corresponding stereoisomeric 1-hydroxydecalincarboxylic acids XII, XIII, and XIV:



In this case, the lower yield of acid XIII is probably explained by the already noted greater hindrance of the carbon chain in trans-1-ethynyl-1-decalol II and the acetyl-1-decalol X prepared from it.

On acetylation of the hydroxydecalincarboxylic acids under mild conditions (refluxing with acetyl chloride in ether [13]), only acetates XV and XVII were isolated, while acid XIII was recovered from the reaction unchanged, and it was not possible to prepare acetate XVI under these conditions.

Convinced by the ease of acetylation of the hydroxyl group in acetylenic alcohols III and V and also in hydroxydecalincarboxylic acids XII and XIV, we assigned to these compounds an equatorial hydroxyl in contrast to trans-1-ethynyl-1-decalol II, in which the hydroxyl is apparently oriented axially.

From a consideration of the data on the rates of hydration of isomeric ethynyldecalols II, III, and V, from a consideration of the ability of the hydration products to form derivatives at the carbonyl group, and from a consideration of the ease of oxidation of acetyldecalols IX, X, and XI with sodium hypobromite, it becomes apparent that the side chains are subjected to the greatest steric hindrance in compounds with axial hydroxyl groups (II, X, and XIII), and that the least steric hindrance is found in compounds with equatorial hydroxyl groups (III, IX, and XII); this, in all probability, is connected with a different degree of shielding of the hydroxyl group by the rings.

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR

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RETENTION OF CONFIGURATION OF THE PROPENYL RADICAL IN REACTIONS OF CIS- AND TRANS-PROPENYLLITHIUM WITH OXO COMPOUNDS

Academician A. N. Nesmeianov, A. E. Borisov and N. V. Novikova

In previous communications [1], we have shown that electrophilic and homolytic exchange reactions at an olefinic carbon atom responsible for cis- and trans-isomers proceeds with retention of the geometric configuration.

This was demonstrated by numerous exchanges of metal for metal.

The present work had as its aim the investigation, from the same point of view, of electrophilic substitution of a metal atom by a carbon atom in reactions of cis- and trans-propenyllithium with oxo compounds.

The propenyllithium isomers were prepared by the action of metallic lithium on the cis- and trans-isomers of propenyl bromide in dry ether. Both propenyl bromide stereoisomers were prepared by dehydrobromination of 1,2-dibromopropane [2], and, after their separation in a column equivalent to 60 theoretical plates, they were immediately introduced into the reaction.

The trans-isomer had a b. p. of 62.5-63° and a n_D^{16} of 1.4561, and the cis-isomer boiled at 57° and had a n_D^{16} of 1.4570. Their configurations are known [3].

Investigation of the infrared absorption spectra of a 15-20% ethereal solution of the propenyllithium stereoisomers showed that the propenyllithium prepared from cis-propenyl bromide had vibrational frequencies at (in cm^{-1}): 700; 726; 736; 845; 890; 922; 1028-1185; 1285; 1350; 1390; 1450; 1480; 1562; 1623; 1852; 1874 – propenyllithium prepared from trans-propenyl bromide had vibrational frequencies at (in cm^{-1}): 736; 845; 890; 922; 975; 1022-1170; 1285; 1302; 1350; 1388; 1450; 1484; 1645; 1960. The characteristic vibrational frequencies for cis-compounds of this type are 700 and 1623 cm^{-1}, and those for their trans-isomers are 975 and 1645 cm^{-1}. On the basis of these data, the propenyllithium prepared from cis-propenyl bromide must be the cis-compound, and the propenyllithium prepared from trans-propenyl bromide must be the trans-compound.

Into an ethereal solution of cis- or trans-propenyllithium was introduced a corresponding amount (calculated on the basis of 0.008 mole) of ketone or aldehyde in 200 ml of dry ether.* After the reaction mixture had been stirred for two hours, decomposed with a saturated solution of ammonium chloride, and dried with potassium carbonate, the reaction product was distilled.

We investigated the products of the reaction of cis- and trans-propenyllithium with acetone, acetophenone, benzophenone, p-chlorobenzophenone and also with acetaldehyde and benzaldehyde.

In each case, from the reaction of cis-propenyllithium with ketones and aldehydes we obtained the corresponding tertiary and secondary alcohols having cis-configurations, while trans-propenyllithium reacted with these same reagents to give the corresponding trans-compounds.

* In all experiments, the propenyllithium was prepared from 10 g (0.008 mole) of propenyl bromide and 1.10 g (0.016 mole) of metallic lithium in dry ether at 5-7°.

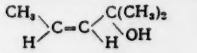
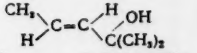
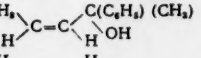
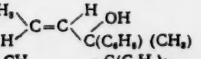
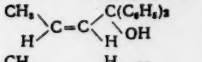
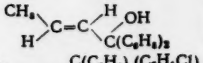
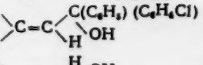
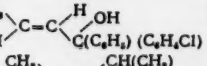
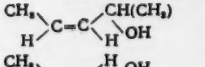
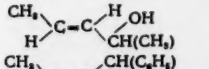
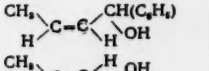
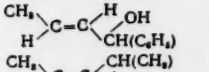
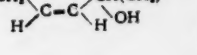
TABLE 1

Vibrational Frequencies of the Infrared Absorption Spectra of the Products of the Reaction of Propenyllithium Stereoisomers with Aldehydes and Ketones (in cm^{-1})

$CH_3CH{=}CH{-}C(CH_3)_2$ $\quad\quad\quad

TABLE 2

Physicochemical Constants of the Products of the Reaction of Propenyllithium Stereoisomers with Aldehydes and Ketones

Starting materials		Reaction temp., °C	Reaction products	Constants of the resulting products						M.p. of p-nitrobenzoate, °C	Yield, %
formula $CH_3CH=CHLi$	aldehyde or ketone			b. p., °C	pressure in mm Hg	n_D^{20}	d_4^{20}	MR found	MR calc.		
Cis-	CH_3COCH_3	−2		60—61	72	1.4352	0.8435	31.00	30.97	53—54.5	51
Trans-		0		65—67	72	1.4328	0.8356	31.14		65—66	54
Cis-	$CH_3COC_6H_5$	−5		80—81	3	1.5310	0.9934	50.52	50.51		68
Trans-		−2		86	4	1.5329	0.9961	50.53			67
Cis-	$C_6H_5COC_6H_5$	0		145	3	1.5901**	1.0757**	70.38	69.94		66
Trans-		−2		152—154*	3	1.5860**	1.0704**	70.31			68,4
Cis-	p-$ClC_6H_4COC_6H_5$	0		165	2	1.6010	1.1774	75.28	74.81		63
Trans-		0		160—162	3	1.5963	1.1708	75.21			62
Cis-	CH_3CHO	0		65,5	70	1.4305	0.8476	26.28	26.35	77.5—78	52
Trans-		0		64—65	74	1.4281	0.8371	26.48		54—55	58
Cis-	C_6H_5CHO	−5		101—102	6	1.5400	1.0109	45.98	45.84	56—57	58
Trans-		−5		102	5	1.5370	1.0039	46.10		98—99	56
		20		63—65	70	1.4301	0.8472	26.27	26.35	77—78	37

*Freezing point, 20.5°.

**Constants measured at 25°.

The assignment of the configurations of the reaction products was made on the basis of the vibrational frequencies of the infrared absorption spectra, which are presented in Table 1.*

Characteristic vibrational frequencies of trans-compounds occur in the region of 960-980 cm^{-1} – out-of-plane C–H vibrations – and in the region of C–C double bond vibrational frequencies, which is higher for trans-compounds than for cis-compounds.

Besides C–C double bond vibrational frequencies, the presence of a vibrational frequency in the region of 700 cm^{-1} and the complete absence of vibrational frequencies in the region of 960-980 cm^{-1} are characteristic of cis-compounds.

It should be noted that reaction products not purified by distillation had precisely the same infrared frequencies.

It is well known that acetylene derivatives catalytically add two atoms of hydrogen in the cis-position [4]; we made use of this property to synthesize individually the cis-isomer of 1-methyl-2-butene-1-ol [3-pentene-2-ol] by partial hydrogenation of methylpropynylcarbinol in the presence of Raney nickel, and thereby additionally confirmed its configuration.

The cis- and trans-isomers of 1,1-dimethyl-2-butene-1-ol [2-methyl-3-pentene-2-ol], 1-methyl-2-butene-1-ol [3-pentene-2-ol], and 1-phenyl-2-butene-1-ol were also identified in the form of their p-nitrobenzoates (see Table 2).

Thus, cis- and trans-isomeric organometallic derivatives of olefins with the metal at the olefinic carbon react with oxo compounds with retention of the configuration of the olefinic radical (as we have previously shown to be the case in carbonation reactions with CO_2 [5]).

The rule, established by us, of retention of configuration of an olefinic radical during electrophilic and homolytic substitution at the olefinic carbon atom has, as would be expected, general significance.

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* The infrared spectra of the first four cis- and trans-isomers (see Table 1) were obtained at our request by L. A. Kazitsyna and G. A. Rudenko (Moscow State University), and those of the remaining three stereoisomers were obtained by V. N. Smorchkovyi (Optical Laboratory of the Institute of Heteroorganic Compounds of the Academy of Sciencies USSR), for which we express our appreciation.

** Orginal Russian pagination. See C.B. Translation.

DEHYDROCYCLIZATION OF n-HEPTANE OVER CHROME-ALUMINA CATALYSTS

M. I. Rozengart and Academician B. A. Kazanskii

One of the peculiarities of chrome-alumina catalysts in the aromatization of paraffinic hydrocarbons is the short synthesis cycle due to the necessity of regenerating the catalyst after several hours of operation. This is connected with deactivation of the catalysts by carbonaceous deposits ("coke") formed on the catalyst surface during the synthesis period.

Our experiments on the dehydrocyclization of n-heptane showed that it is possible to prepare such catalysts which will operate continuously without regeneration for a long period of time, approaching 27 hours, while maintaining an average aromatics yield of 67% over this period. After 100 hours operation with periodic regenerations, the length of the synthesis period decreased to 10-12 hours, and did not change further over the next 115-117 hours of operation. After 215-217 hours of operation, the surface of the catalysts decreased by a factor of three and the pore volume by a factor of one and a half. Along with this, the total yield of reaction products and the yield of toluene per pass of n-heptane through the catalyst changed insignificantly. It may be assumed that one of the reasons for this is that, under our conditions (515°, 0.3 hours^{-1} space rate), the dehydrocyclization reaction proceeds over active catalysts in the diffusion, not the kinetic, region. Experiments with samples of catalysts of different granule size confirmed this assumption.

EXPERIMENTAL

The experiments were carried out in a vertical block furnace in which were simultaneously placed two 18 mm internal diameter reaction tubes of refractory glass. A 15.5 mm external diameter insert, made from a tube of the same glass by sealing at both ends, was inserted in the reaction tube over the catalyst layer. The temperature was measured with a chromel-alumel thermocouple, the hot junction of which was placed in the block. The heptane was fed by means of a syringe [1]. The reaction products were collected in a water-cooled receiver and in a following coil trap which was placed in a Dewar containing a mixture of dry ice and acetone.

Commercial heptane was treated, as usual, with concentrated sulfuric acid, and was then distilled in a column equivalent to 24 theoretical plates. The resulting heptane had the following constants: b. p. 98.4°/760 mm, n_D^{20} 1.3878, d_4^{20} 0.6834.

The chrome-alumina catalysts, which were promoted with potassium ion, had the same composition (chromic oxide 15, aluminum oxide 82, potassium oxide 3 mole %), but differed somewhat in method of preparation. Catalysts 149 and 162 were used in the form of granules of 3-5 mm diameter, and Catalyst 187 was in the form of granules of 0.5-1 mm and 3-5 mm diameter.

The content of aromatics in the catalyzates was calculated from the index of refraction by means of a curve showing the relation between the refractive index and composition of heptane-toluene mixtures; in certain cases, the aromatics content was determined from the dispersion. Numerous analyses of catalyzates obtained, during the course of our investigations, by aromatization of individual hydrocarbons (n-hexane, n-heptane, n-octane, cyclohexane, and methylcyclohexane) over different catalysts confirmed that the refractometric method of determining aromatics is sufficiently accurate. We were able to show that the difference between the content of aromatics as determined from the refractive index and that determined from the dispersion taking into account the unsaturates determined by bromine number was less than 5% when the bromine number, in the case of heptane, did not exceed 15.

Protracted testing of the catalysts• (catalyst 149 was tested over a period of 217 hours and Catalyst 162 over a period of 215 hours) was carried out at 510° using 20 ml of catalyst. The index of refraction and the yield were determined for catalyzates collected over 4-hour periods. The catalysts were regenerated when the index of refraction of the 4-hour catalyzates dropped to 1.4500 or somewhat lower. Regeneration with air was carried out at the temperature of the experiment, determined by the thermocouple in the block; prior to and after regeneration, the catalyst was flushed with nitrogen for 5 minutes. In order to activate freshly charged catalysts, it was necessary to carry out 1-3 two-hour experiments with subsequent regenerations, following which the catalysts acquired high activity. In Table 1 are presented the results of some experiments with long synthesis periods, experiments with the same catalysts after the length of the synthesis period had decreased, and also the final experiments testing Catalysts 149 and 162.

TABLE 1

Aromatization of n-Heptane over Catalyst 149 (Experiment Series 380) and Catalyst 162 (Experiment Series 382) at 515° and a Space Rate of 0.3 Hours^{-1}

Expt. No.	Synthesis time, hours	Prop. of catalyzates coll. in 4-hr periods		Yield, wt.% (calc. on n-C_7H_{16})		
		n_D^{20}	bromine no.	catalyzate	aromatics	unsaturates
Catalyst 149						
6	1—4	1.4680	10.1	84	67	5
	5—8	1.4685	10.9	87	70	6
	9—12	1.4659	9.6	86	68	5
	13—16	1.4704	13.9	77	64	7
	17—20	1.4580	19.0	77	55	9
			Average		65	
8	1—4	1.4735	—	78	65	
	5—8	1.4768	—	76	66	
	9—11	1.4547	—	85	58	
			Average		63	
15	1—4	1.4571	8.8	94	66	5
	5—8	1.4601	9.8	91	67	5
	9—10	1.4492	12.5	82	52	6
			Average		64	
Catalyst 162						
4	1—4	1.4843	4.1	79	73	2
	5—8	1.4882	3.6	79	75	2
	9—12	1.4796	6.0	84	74	3
	13—16	1.4756	7.9	81	68	4
	17—20	1.4703	8.6	81	65	4
	21—24	1.4645	10.8	76	59	5
	25—27	1.4529	13.3	83	55	7
			Average		67	
7	1—4	1.4739	—	85	71	—
	5—8	1.4632	—	84	64	—
	9—12	1.4535	—	82	55	—
			Average		63	
10	1—4	1.4681	5.6	78	63	3
	5—8	1.4650	8.0	82	64	4
	9—12	1.4480	12.2	78	48	6
			Average		58	

As seen from Table 1, in Experiment 6, Catalyst 149 retained high activity for a period of 20 hours of continuous operation without regeneration; the average yield of aromatics during this period was 65%, calculated on the heptane fed. Further synthesis periods dropped to 10-11 hours, and the yield of aromatics dropped to 63%. In Experiment 4, the synthesis period of Catalyst 162 was 27 hours with an average yield of aromatics of 67%. As in the previous case, the synthesis period then dropped to 12 hours, and the average yield of aromatics dropped to 58%. As is apparent from the bromine number, the content of unsaturates in the catalyzates was small and varied only slightly, increasing toward the end of a synthesis period simultaneously with the drop in aromatics yield.

• O. D. Sterligov, P. S. Pavlova, A. A. Frolov, V. A. Ovodova, G. S. Taits and T. V. Vasina took part in the protracted, day-round tests. Z. F. Kuznetsova took part in this and in a number of other parts of the work.

Results of the distillation and analysis of catalyzates obtained at the beginning, in the middle, and at the end of operations with Catalyst 149 also indicate a systematic decrease in toluene content during the testing from 71 wt. % for a mixture of the catalyzates from the first six experiments to 69% for a mixture of the catalyzates from the last five experiments. A small amount of benzene was simultaneously formed (about 3%). The content of organic material on Catalysts 149 and 162 was 4% after an 8-hour synthesis period and subsequent purging with nitrogen for 20 minutes at the temperature of the experiment. The amount of organic material on Catalyst 140 was determined both during the testing by analysis of the effluent gas during regeneration and by combustion of a sample of the catalyst collected at the end of a test; the organic material content of Catalyst 162 was determined only by the last method.*

Measurement of the surfaces of Catalysts 149 and 162 was carried out by adsorption of benzene vapors from a stream of air, using the method described for oxide catalysts by A. M. Rubinshtein and A. V. Afanas'ev [2]. It was shown that during the course of the entire test period with 14 regenerations, the surface of Catalyst 149 decreased from 217 to 69 sq. m./g, and that of Catalyst 162 (9 regenerations) decreased from 332 to 107 sq. m./g. The pore volume of Catalyst 162, calculated from the results of the adsorption of benzene vapors by the catalyst in a desiccator over pure benzene, changed from 0.265 to 0.175 cc/g. Such a change in the physical structure of our catalysts is characteristic of aluminum oxide or of catalysts prepared from it when subjected to the action of high temperature, sometimes in conjunction with water vapor [3, 4], which can be formed in the first moments of regeneration and in the beginning of experiments after regeneration.

TABLE 2

Aromatization of Heptane Over Catalyst 187 at 510° with a Run Time of 4 Hours and a Heptane Feed Rate of 6.5 ml per Hour

Expt. No.	Weight of Catalyst, g	Weight rate, hours^{-1}	n_D^{20} of catalyzate	Bromine no. of catalyzate	Yield, wt. % (of n-C_7H_{16})		
					catalyzate	aromatics	unsaturates
0.5-1 mm Granule							
414[1]	8.78	0.48	1.4424	14.4	78	45	6.9
414[2]	8.78	0.48	1.4452	—	79	47	—
421	4.39	1.08	1.4277	16.5	88	39	8.9
423	4.39	1.16	1.4270	16.8	89	38	9.2
425	2.11	2.25	1.4089	17.2	96	24	10.1
3-5 mm Granule							
413[1]	8.78	0.50	1.4417	18.3	76	43	8.5
413[2]	8.78	0.50	1.4389	—	79	42	—
417	4.39	1.09	1.4183	19.7	91	31	11.0
424	4.39	0.97	1.4175	—	93	31	—
426	2.11	2.08	1.4038	—	96	18	—
427	2.11	2.08	1.4058	16.1	94	19	9.5

Experiments with two samples of Catalyst 187 of different granule size were carried out at different space rates and at 510° using 4-hour periods with subsequent regeneration. Variation in the space rate was accomplished by changing the amount of catalyst charged to the tube (2.11, 4.39, and 8.78 g) while maintaining the same heptane charge rate (6.5 ml/hour). In parallel experiments with catalysts of different granule size, the same weight of catalyst was charged each time. Since the bulk density of the 0.5-1 mm catalyst was 1.02 and that of the 3-5 mm catalyst was 0.88, the space rate was different in parallel experiments; however, the weight rate, i.e., the amount of liquid, expressed in grams, passed through a gram of catalyst in an hour, was practically the same in parallel experiments. The results of these experiments are presented in Table 2 and in Figure 1.

* The determination of organic material by combustion was carried out in the Laboratory of Microanalysis of the Institute of Organic Chemistry AN SSSR, which is supervised by V. A. Klimova.

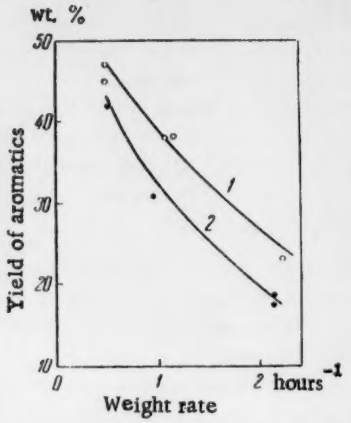

Fig. 1. Aromatization of heptane over Catalyst 187 with different granule diameters (1 – 0.5-1 mm, 2 – 3-5 mm) at 510° and various weight rates.

With an increase in weight rate from 0.5 to 2.15 hours^{-1}, the increase in the yield of catalyzate was practically the same, from 78 to 96%, in each of two parallel experiments in which the granule size of the catalyst differed; with the catalyst having a granule size of 0.5-1 mm the yield of aromatics in the catalyzate decreased from 46 to 24%, while the decrease was from 42.5 to 18.5% with the catalyst having a granule size of 3-5 mm. Both curves showing the relation of aromatics yield to heptane weight rate had the same direction, the curve for the coarser catalyst lying below the other. The yield of unsaturates increased from 6.9 to 10.1% in the first case and from 8.5 to 9.5% in the second.

It follows from these results that the granule size of the catalyst affects the yield of aromatics. According to existing views [5-7], dependence of the yield of products of a reaction on the granule size of the catalyst is proof that the reaction proceeds in the so-called diffusion region; i.e., diffusion of the components of the reaction mixture affects the reaction rate. Consequently, aromatization of heptane over promoted chrome-alumina catalyst proceeds in the diffusion region.

In this connection, it should be noted that an effect of catalyst granule size has also been noted for the dehydrogenation over chrome-alumina catalyst of n-butane [8] and of cyclohexane [9]. This phenomenon, which, as we have seen, is general for different reactions of saturated hydrocarbons over chrome-alumina catalysts, can apparently be explained on the basis that at the relatively high temperatures (450-550°) at which these conversions proceed over oxide catalysts, the rate of the reaction becomes equal to or exceeds the rate of diffusion of the hydrocarbons into the catalyst.

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR

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POLYMERIZATION OF ISOBUTYLENE BY THE ACTION OF BORON TRIFLUORIDE ADSORBED ON SILICA GEL

Academician A. V. Topchiev and L. A. Aliavdina

The present communication presents the results of an investigation of the polymerization of isobutylene in the presence of boron trifluoride on silica gel; this reaction was first carried out by us [1] with the preparation of low-molecular-weight polymers of isobutylene, i. e., diisobutylene and triisobutylene.

In the present work, the dependence of isobutylene conversion and product distribution on space rate, temperature, catalyst age, and amount of boron trifluoride adsorbed on the silica gel was investigated.

The polymerization of isobutylene was studied at temperatures of 20, 70, 100, and 150° and at isobutylene feed rates of 6 and 30 liters/hour, which corresponds to space rates of 60 and 300 $hours^{-1}$. The experiments were carried out at atmospheric pressure.

The boron trifluoride was prepared by the reaction at elevated temperature of 1 part by weight of B_2O_3, 2 parts by weight of CaF_2, and 10 parts by weight of 5% oleum. The boron trifluoride was passed through a wash bottle containing sulfuric acid and boric oxide to remove traces of water and hydrogen fluoride. The isobutylene, which contained 98% unsaturates, was obtained by catalytic dehydration of isobutyl alcohol (b.p 107°) over aluminum oxide at 400°.

The isobutylene polymerization was carried out in a reactor 40 cm long and 2.6 cm in diameter, which was fitted with an electrical heater. The downstream end of the reactor was connected to a tube 12 cm long containing pieces of NaOH in order to remove boron trifluoride, thereby preventing polymerization outside the reactor.

50 liters of isobutylene and 100 cc (or 45 g) of dry, ShSK brand silica gel, on which 3.5-4 g of boron trifluoride had been adsorbed at 150°, were used for each experiment. The catalyst – boron trifluoride on silica gel – was placed in the reactor, and the isobutylene was then passed into the reactor from a gasometer. In the adsorption of the boron trifluoride on the silica gel, the samples were brought to constant weight. The reactor was cooled with water during the experiments at 20°. The collected polymer was washed, dried, and distilled in a column.

TABLE 1

Type of experiment	Amt of isobutylene, liters	Space rate, $hours^{-1}$	Conversion, %	Temp, °C	Amt of BF_3, g	d_4^{20}	n_D^{20}	Octane number
Without BF_3 in feed	50	60	97	20	13	0.7940	1.4471	84
	50	60	97	20	3.5	0.7790	1.4405	
	50	60	95.5	70	4	0.7581	1.4309	
	50	60	86	100	3.5	0.7412	1.4233	
	50	300	32	100	3.5	0.7331	1.4190	
	50	60	65	150	4	0.7376	1.4195	85
With BF_3 in feed	50	60	30	150	5	0.7165	1.4120	

Figure 1 shows that at a space rate of 60 hours^{-1}, the conversion of isobutylene decreased from 97 to 65% with an increase in temperature. Obviously, the surface of silica gel holds boron trifluoride less tightly at 150° than at 20, 70, and 100°. With an increase in temperature, the amount of the fraction boiling above 185° also dropped, from 52 to 8%, while the fraction boiling at 98-126° increased and reached 37%.

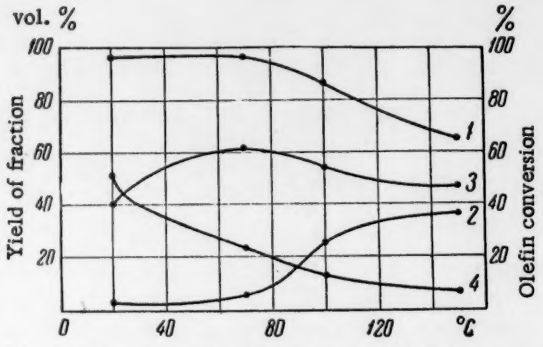

Fig. 1. The effect of temperature on isobutylene conversion (1) and on the yield of polymer fractions at a space rate of 60 hours^{-1} with a catalyst of BF_3 on silica gel. Fractions: 2 – 98-126°; 3 – 170-185°; 4 – >185°.

Thus, a lighter polymer is obtained at the higher temperatures, as is also confirmed by the data of Table 1, which presents the physical properties of the polymers obtained.

Figure 2 presents curves obtained by fractional distillation of two polymers. The first polymer, which was obtained with a catalyst containing 13 g of BF_3 (adsorption at 20°), is significantly heavier than the second, which was obtained with 3.5 g of BF_3 on silica gel (see Table 1). Consequently, the polymerization proceeds more deeply with an increase in the amount of BF_3 adsorbed on the silica gel.

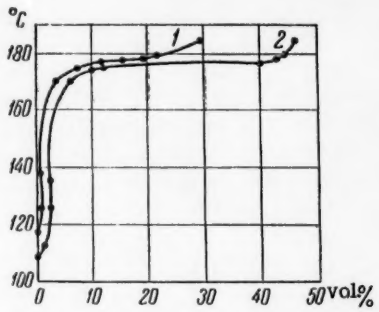

Fig. 2. Relationship between the amount of BF_3 on the silica gel and the fractional composition of isobutylene polymer obtained at 20° and a space rate of 60 hours^{-1}: 1 – 13 g, 2 – 3.5 g.

It is seen from Figure 3 that the polymer formed at a space rate of 300 hours^{-1} contained 11% more of the fraction boiling at 98-126°, 9% less of the fraction boiling at 170-185°, and 5% less of the fraction boiling above 185° than did the polymer formed at a space rate of 60 hours^{-1}.

It follows from the material presented that the degree of polymerization of isobutylene will decrease with an increase in space rate or a decrease in time of contact with the boron trifluoride.

The polymerization of isobutylene was also studied at 150° with a feed containing boron trifluoride, which was derived from the molecular compound $K_2SO_4 \cdot BF_3$, first used by us for this reaction [2]. This compound was obtained by the action of boron trifluoride on calcined K_2SO_4 at 235° [3]. The samples were brought to constant weight.

45 g of silica gel, 50 liters of isobutylene, and 17.8 g of $K_2SO_4 \cdot BF_3$, containing 5 g of boron trifluoride, were used in each experiment. The silica gel was placed in the reactor, and the isobutylene was then fed from a gasometer at a space rate of 60 hours^{-1} along with boron trifluoride from the $K_2SO_4 \cdot BF_3$, which was decomposed to K_2SO_4 and BF_3 at 360-390°in an electric furnace.

The physicochemical constants of the resulting polymer were: d_4^{20} 0.7165, n_D^{20} 1.4120, bromine number 132, molecular weight 119.7, unsaturates 98.7% (the molecular weight was determined cryoscopically). It can be seen from the data of Table 1 that the polymer obtained with a feed containing boron trifluoride was lighter than the polymer obtained without boron trifluoride in the feed.

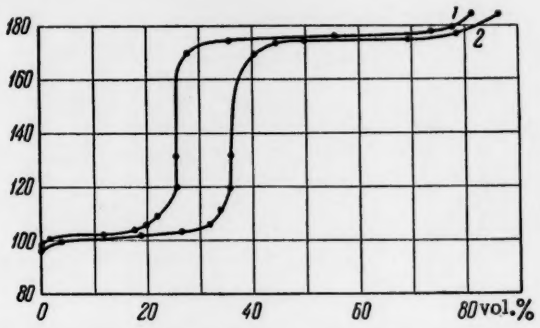

Fig. 3. Dependence of fractional composition of isobutylene polymer on space rate; polymer obtained at 100° with a catalyst of BF_3 on silica gel: 1 – 60 hours^{-1}; 2 – 300 hours^{-1}.

In Table 2 are reported the results of a spectral analysis of certain fractions of polymers which were investigated by Raman spectroscopy.

TABLE 2

Catalyst	Temp., °C	Space rate, hours^{-1}	Fraction, °C	Chemical composition	B.p. from literature [4], °C
BF_3 on silica gel	20	60	98—106	2,4,4-trimethyl-1-pentene	101.36
				2,4,4-trimethyl-2-pentene	104.85
	20	60	108—120	3,4,4-trimethyl-2-pentene	112.3
				2,3,4-trimethyl-2-pentene	116.26
				2,3,4-trimethyl-1-pentene	117.15
	150	60	98—106	2,4,4-trimethyl-1-pentene	101.36
				2,4,4-trimethyl-2-pentene	104.85

The data of Table 2 show that the polymerization of isobutylene was accompanied by isomerization, as a result of which 3,4,4-trimethyl-2-pentene and, subsequently, 2,3,4-trimethyl-2-pentene and 2,3,4-trimethyl-1-pentene appeared.

Catalyst life was investigated at 20 and 100° and a space rate of 60 hours^{-1}. In the first case, the adsorption

of the boron trifluoride on the silica gel was carried out at 20°. The resulting catalyst consisted of 14 g of BF_3 on 45 g of silica gel. 1038 liters of isobutylene was used in the experiment, which continued for 158.3 hours.

Figure 4 shows the very high conversion of isobutylene obtained, from 98% to 90% at the end of the experiment. After 158.3 hours of operation, 2217 g of polymer had been obtained at an average conversion of 94.7%. The physical constants of the polymer (average sample) were: d_4^{20} 0.7682, n_D^{20} 1.4335, octane number 85. The octane number was determined by the motor method using a "Vokesh" apparatus.

Catalyst life was also studied at 100°. The catalyst consisted of 7.5 g of boron trifluoride on 45 g of silica gel (adsorption at 100°). For this investigation, which ran for 33.3 hours, 200 liters of isobutylene was used. 335 g of polymer was obtained at an average conversion of 74.3%. The physical constants of the polymer obtained at the end of the experiment were: d_4^{20} 0.7422, n_D^{20} 1.4238.

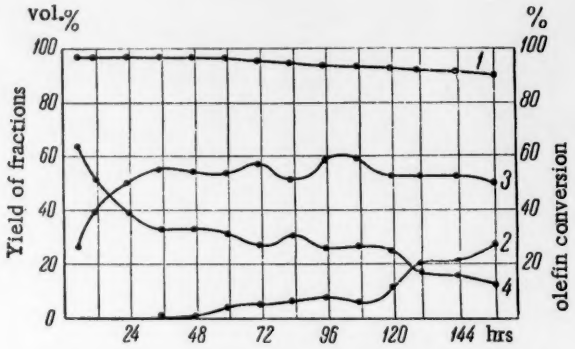

Fig. 4. Effect of catalyst age on isobutylene conversion (1) and yield of polymer fractions; polymerization at 20° and a space rate of 60 $hours^{-1}$ over BF_3 on silica gel. Fractions: 2 – 100-126°; 3 – 170-185°; 4 – > 185°.

From the data presented, it follows that a catalyst of boron trifluoride on silica gel is active for a long time and acts effectively at 100°. The high isobutylene conversion at the end of the investigation at 20° demonstrates the very long and effective life of the investigated catalyst, which was operating after 158.3 hours without regeneration.

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DETERMINATION OF THE PURITY AND CRYSTALLIZATION TEMPERATURE OF SOME HYDROCARBONS USING 1-2 ML SAMPLES

A. G. Anikin and G. M. Dugacheva

(Presented by Academician B. A. Kazansky, November 30, 1957)

Of the many published works on the determination of the purity of organic compounds from the crystallization curves, the investigations of Rossini [1, 2] are apparently the most accurate and have the firmest theoretical foundation. Unfortunately, newly synthesized organic materials are frequently obtained in very small amounts and the method of Rossini is not practicable, since rather large amounts of material (40-50 ml) are required for purity determinations by this method.

This is the reason that attempts have been made to decrease the size of the sample without violating the basic requirements of the Rossini method. Of the conditions required by the Rossini method, the most essential is the requirement of maintaining thermodynamic equilibrium between the liquid and crystalline phases during the crystallization process.

This condition is fulfilled in practice by stirring the material, in the majority of cases by means of an ordinary stirrer. This condition makes it difficult to decrease the size of the sample. A number of attempts in this direction have been made, the most serious of which is apparently the work of Peshkov [3], who, by changing the construction of the Rossini stirrer and by replacing the resistance thermometer by a copper – constantan thermocouple, was able to decrease the sample size to 7-8 ml and to obtain crystallization curves of the material with an accuracy of up to $\pm$ 0.01°.

In a joint effort of Peshkov with Tilicheev and Iuganova [4], the volume of the sample was reduced to 3.5 ml, but in this case the stirrer was replaced by a copper grid mounted inside the reaction cell to equalize the temperature gradients, and this device is a poor substitute for a stirrer.

In the work of other investigators attempting to decrease the amount of material being investigated, stirring was not used [5]; this violates Rossini's condition, and makes the use of his method of calculation unjustified.

Our work was devoted to an attempt to reduce the sample size to 1-2 ml without violating Rossini's condition of thermodynamic equilibrium between crystals and liquid during crystallization. This object was attained by decreasing the size of the reaction cell and by certain changes in the construction of the stirrer.

The simplest Rossini stirrer is a nichrome wire curled into a spiral at one end [1]. Such a stirrer is not suitable for working with small amounts of material, since the clearance between the thermocouple sleeve and the inner walls of the reaction cell is very small, and the material becomes smeared on the walls of the cell. As a result of this, during the crystallization the thermocouple junction is not in the material, but is in the vapor space formed between the walls of the thermocouple sleeve and the material smeared on the walls of the cell, so that the thermocouple measures the temperature of this vapor space and not that of the material being investigated, which leads to altered results.

Two forms of stirrer were used in the present work. In one case, the stirrer consisted of a nichrome wire bent into a closed circle of the diameter of the reaction cell (Figure 1a), and in the other case, three extensions of the same nichrome wire were soldered to the ring at points spaced equally around the ring (Figure 1b), these extensions also stirring the material.

The stirrer was motor-driven, and moved up and down with a 20- to 25-mm stroke at a rate of 60-85 strokes per minute.

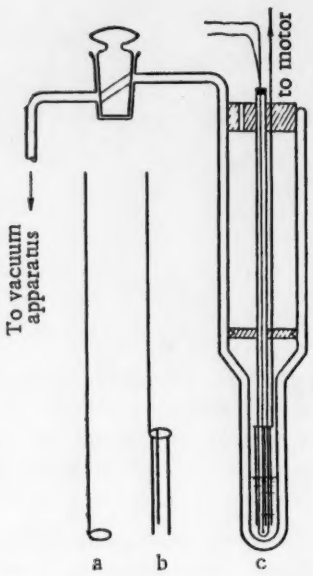

Fig. 1.

Basically, the measurements remained the same as in the previous work [6]. The crystallization temperature was measured with a copper-constantan thermocouple which had been calibrated against a standard resistance thermometer. In contrast to the former one, the thermocouple was made of fine wire having a diameter of approximately 0.05 mm, and it was inserted into a sleeve with an internal diameter of 2.5 mm. A sleeve of such a small diameter is comparatively fragile, and the thermocouple assembly had to be well centered to avoid contact with the stirrer during stirring. For this purpose, the reaction cell was constructed with its upper part wider than the lower part which contained the substance being investigated (Figure 1c). A well-centered plug was in the upper part of the cell, and the thermocouple was also fixed in the plug which closed off the cell containing the sample. When working with materials which crystallized at temperatures of from −65 to −140°, in which case the coolant was liquid nitrogen, a vacuum of 10^{-2}–10^{-3} mm Hg was created in the jacket of the reaction cell to slow down the rate of cooling. The crystallization curves were automatically recorded with an accuracy of ± 0.05° on the chart of a modified EPP-09 recording potentiometer [8], which served as a null instrument for a PMS-48 low-resistance potentiometer; the latter bucked out part of the e.m.f. developed by the thermocouple prior to recording of the curve by the recorder, and measured the thermal e.m.f. at the required point of the curve.

Owing to the small amount of the material being investigated, the plateau of the curve obtained was not large, and, therefore, it was not convenient for use in the calculations. In order to obtain a good curve, it was necessary to increase the chart speed of the recorder by a factor of two to three over that used for recording curves with samples of 7-10 ml. Thus, for n-octane the chart speed had to be increased from 180 to 360 mm/hour when the sample volume was decreased from 10 to 1.5 ml. The increase was from 180 to 720 mm/hour in the case of n-heptane.

The amount of impurities in the material and the crystallization temperature of the material in the complete absence of impurities were determined by the formulas given by Rossini [1, 9, 10]. The simplest of these [9] are:

$$N_2 = A(t_{f_0} - t_f), \quad (1)$$

where N_2 is the mole fraction of impurity, A is the cryoscopic constant, t_{f_0} is the crystallization temperature of the absolutely pure material (i. e., in the complete absence of impurities), t_f is the crystallization temperature of the original sample, and

$$t_{f_0} = t_f + (t_f - t_r), \quad (2)$$

where t_r is the crystallization temperature of the original material at that point on the curve at which half of the material has crystallized.

The cryoscopic constant A was determined by measuring the freezing point depression of the original sample due to the addition of a measured amount of an appropriate artificial impurity [9], one for which the resulting solution obeys Raoult's law. We then have the following relation:

$$A = \frac{N_2^*(1 + {}^1/_2 N_2^*)}{t_f - t_f'}, \qquad (3)$$

where t_f^* is the crystallization temperature of the original sample containing the artificial impurity, and N_2^* is the mole fraction of the artificial impurity.

Five hydrocarbons were investigated by the method described: n-hexane,* n-heptane, n-octane, methylcyclopentane,** and 2,5-dimethylhexane***; 1.2-2 ml samples were used. For all of these substances, the amount of impurity and the crystallization temperature of the original sample were determined, and the crystallization temperature of the absolutely pure substance was calculated from the experimental data. The reproducibility of the recrystallization curves of n-hexane, n-heptane, n-octane, and 2,5-dimethylhexane was ± 0.05°, and that of methylcyclopentane was ± 0.1°. The results obtained are presented in Table 1.

TABLE 1

Substance	Sample size, ml	A moles/degree		Freezing point, °C			Am't of impurities, mole % (authors' data)
		authors' data	lit. data [2]	orig. sample (authors' data)	absolutely pure		
					authors' data	lit. data [2]	
n-Hexane	1.2	0.050	0.0495	— 95.63	— 95.30	— 95.347	1.60
n-Heptane	2.0	0.0504	0.0507	— 90.98	— 90.57	— 90.610	2.05
	10.0	0.050		— 91.00	— 90.58		2.10
n-Octane	1.4	0.0544	0.0531	— 56.94	— 56.73	— 56.798	1.15
	8.0	0.050		— 56.97	— 56.73		1.20
2,5-Dimethylhexane	1.2	0.0477	0.0467	— 91.37	— 91.21	— 91.200	0.75
	5.0	0.0480		— 91.38	— 91.20		0.80
Methylcyclopentane	1.5	0.0455	0.0488	—142.65	—142.43	—142.455	1.00
	6.0	0.0454		—142.68	—142.46		1.00

For verification and comparison, the same samples of the enumerated substances were investigated in amounts of 6-10 ml at the same time. The divergence of the results obtained when working with 1.2-2 and with 6-10 ml samples did not exceed the experimental error.

Our values for the crystallization temperatures of the absolutely pure materials and our values for the cryoscopic constants of the materials investigated, both for samples of 1.2-2 ml and for samples of 6-10 ml, and the literature values of the crystallization temperatures of the absolutely pure substances and the cryoscopic constants for these same substances [2] are in good agreement within the indicated limits of accuracy (Table 1).

Thus, the feasibility of determining the purity of organic materials with samples of 1-2 ml has been demonstrated.

M. V. Lomonosov Moscow State University

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* Obtained from M. B. Turova, Moscow University.

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TYPES OF STRUCTURAL DIAGRAMS OF TERNARY SYSTEMS BASED ON TITANIUM

I. I. Kornilov and P. B. Budberg

(Presented by Academician I. I. Cherniaev, October 11, 1957)

The previously established nature of the chemical interaction of titanium in binary systems [1-3] is also applicable in considering the case in which titanium simultaneously interacts with two or more components. As was shown previously for titanium alloys, the chemical nature of the reacting elements, their position in the periodic system, the ratio of atomic radii, and the type of crystal lattice are reflected in the structural diagrams of binary systems[1, 3]. Undoubtedly, these factors must determine the nature of the interaction of titanium in ternary metallic systems and, consequently, the types of structural diagrams of ternary systems based on titanium.

From the above-enumerated conditions, and taking into account the structural diagrams of binary systems, the formation of the following types of structural diagrams of ternary systems based on titanium can be demonstrated.

1. When titanium simultaneously interacts with its analogs – zirconium and hafnium – the structural diagram is one in which the ternary system forms continuous solid solutions of the α- and β- modifications of titanium. As is well known, these elements of Group VI also have two allotropic modifications, α- and β-, analogous to the titanium modifications, which leads to the formation in the binary systems Ti–Zr, Zr–Hf, and Ti–Hf of continuous solid solutions both of the α- and of the β-modifications. This ternary system has not been studied experimentally, but from the nature of the interactions in the corresponding binary systems, the structural diagram of the ternary system Ti–Zr–Hf can be represented in this form, as shown in Figure 1. It is the sole system of this type.

2. A structural diagram of a ternary system with continuous solid solutions of β-titanium and limited solid solutions of α-titanium (Figure 2) can be obtained by the simultaneous interaction of titanium with any two of the four metals of Groups V and VI of the periodic system V, Nb, Ta, and Mo. These elements have greatly differing (with respect to titanium) atomic radii and crystal lattices which are isomorphous with the lattice of β-titanium. All six ternary structural diagrams based on titanium and the four elements enumerated above belong to this type. At the present time, only two systems of this type have been investigated: Ti – Nb – – Mo and Ti – V – Nb [4].

3. A structural diagram with an eutectoid reaction of alloys rich in titanium arises by the interaction of titanium with elements which lower the temperature of its polymorphic transformation and which cause an eutectoid decomposition of the β-phase. These elements are H, Cu, Ag, Au, Pb, Si, Cr, W, U, Mn, Fe, Co, and the metals of the platinum group – 16 elements in all.

These elements are distributed among Groups I, IV, VI, VII, and VIII of the periodic system, and they form not only limited solid solutions, but also metallic compounds with the α- and β-modifications of titanium. The presence of similar compounds in the corresponding binary systems makes it possible to carry out triangulation in the ternary system and to investigate independently the secondary ternary systems containing titanium.

The general form of the structural diagram of the 3rd type is presented in Figure 3. In all, there are 120 similar systems.

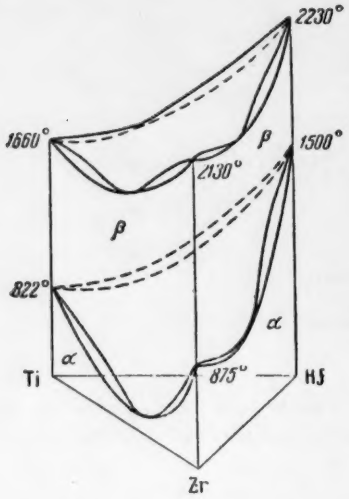

Fig. 1. Ternary system of continuous solid solutions of α- and β-titanium.

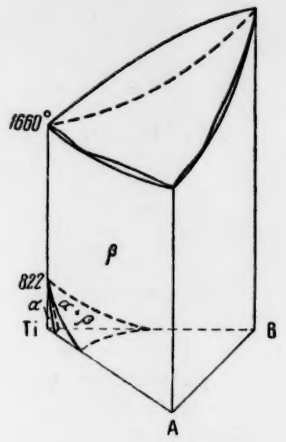

Fig. 2. Ternary system with continuous solid solutions of β-titanium and limited solid solutions of α-titanium.

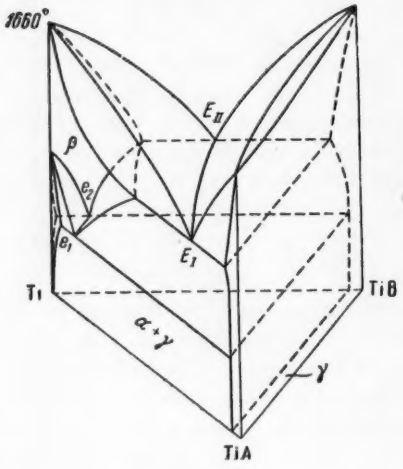

Fig. 3. Ternary system with eutectoid reaction.

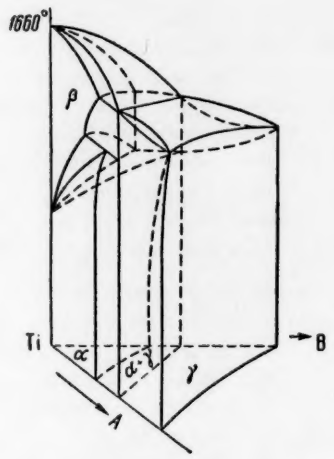

Fig. 4. Ternary system with peritectoid reaction.

4. A structural diagram with peritectic and peritectoid types of reactions of alloys rich in titanium is obtained when titanium reacts simultaneously with elements which raise the melting point and the temperature of the polymorphic transformation of titanium (C, N, O) or with elements which lower the melting point but raise the temperature of the polymorphic transformation of titanium (Al, B, Ge, Sn). A structural diagram with this type of interaction of the components is presented in Figure 4. In all, there are 21 systems of this type. These systems are Ti--C- N, Ti-Al-Sn, etc.

5. The fifth type of structural diagram of ternary systems corresponds to the case where one of the components forms a continuous series of solid solutions with α- and β-titanium, and the second component forms

continuous solid solutions only with β-titanium and limited solid solution with α-titanium; i. e., there is a combination of the 1st and 2nd types of binary diagrams [1]. Ti–Zr–V and Ti–Zr–Nb, for example, are such systems. There is a total of 8 ternary systems of this type.

6. The sixth type of structural diagram of ternary systems arises as a result of a combination of the 1st and 3rd types of binary systems; i. e., when one of the components forms continuous solid solutions with α- and β-titanium, and the second component lowers the temperature of the polymorphic transformation of titanium and causes an eutectoid decomposition of the β-phase. An example is the system Ti–Zr–Cu. The total number of ternary systems of this type is 32.

7. The seventh type of structural diagram of ternary systems of titanium arises when one of the components forms continuous solid solutions with α- and β-titanium, and the second raises the temperature of the polymorphic transformation of titanium with a subsequent peritectic or peritectoid reaction; i. e., a combination of the 1st and 4th types of binary diagrams. An example is the system Ti–Zr–Al. There is a total of 14 systems of this type.

8. The eighth type of structural diagram of ternary systems is formed as a result of a combination of the 2nd and 3rd types of binary diagrams, i. e., when one of the components forms continuous solid solutions only with β-titanium, and the second lowers the temperature of the polymorphic transformation of titanium and causes an eutectoid decomposition of the β-phase. An example is the system Ti–V–Cu. There is a total of 64 systems of this type.

9. The ninth type of structural diagram of ternary systems corresponds to a combination of the 2nd and 4th types of binary systems, i. e., when one of the components forms continuous solid solutions only with β-titanium, and the second raises the temperature of the polymorphic transformation of titanium with a subsequent peritectic or peritectoid reaction. Ti–Mo–Al, Ti–V–Al, etc. belong to this type of system. There is a total of 28 systems of this type.

10. The tenth type of structural diagram of ternary systems is formed as a result of a combination of the 3rd and 4th types of binary diagrams, i. e., when one of the components lowers the temperature of the polymorphic transformation of titanium and causes an eutectoid decomposition of the β-phase, and the second component, on the contrary, raises the temperature of the polymorphic transformation of titanium, leading to peritectic and peritectoid reactions. An example is the system Ti–Cu–Al. There is a total of 112 systems of this type.

The types of structural diagrams considered above encompass all of the forms of interaction of titanium in ternary systems based on it. Experimental investigations of certain titanium-containing ternary systems [4-6] confirm the correctness of the classification presented above.

The examples, presented above, of the basic types of structural diagrams of ternary systems based on titanium are important. They orient investigators during the setting-up of a problem and the selection of specific ternary systems for experimental study, and they also depict, in general form, the nature of the interaction of the elements in the selected ternary system. These types of structural diagrams also offer the possibility of previously setting a goal of obtaining specific compositions having one structure or another.

In accordance with the assigned composition and structure, it is possible to count on obtaining specific physicochemical and mechanical properties of alloys based on the ternary systems, i. e., to solve the problem of obtaining ternary alloys of titanium with previously assigned properties.

A. A. Baikov Institute of Metallurgy
Academy of Sciences USSR

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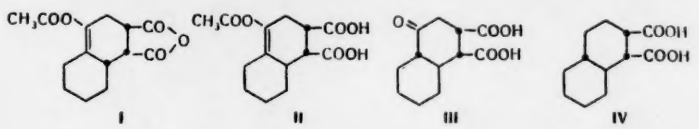
STEREOCHEMISTRY OF THE DIENE CONDENSATION OF 1-α-ACETOXYVINYL-Δ^1-CYCLOHEXENE WITH MALEIC ANHYDRIDE

Academician I. N. Nazarov,* V. F. Kucherov, V. M. Andreev and G. M. Segal'

As was shown in one of our previous communications [1], the condensation of 1-α-acetoxyvinyl-Δ^1-cyclohexene with maleic anhydride in boiling benzene gives the liquid addition product I, the hydrolysis of which with water forms only the anti-cis-4-acetoxy-Δ^4-octalin-1,2-dicarboxylic acid II in 85% yield. Its configuration was demonstrated by conversion to the trans-anti-cis-4-keto acid III, which gives on Clemmensen reduction the well known trans-anti-cis-decalin-1,2-dicarboxylic acid IV.



I II III IV

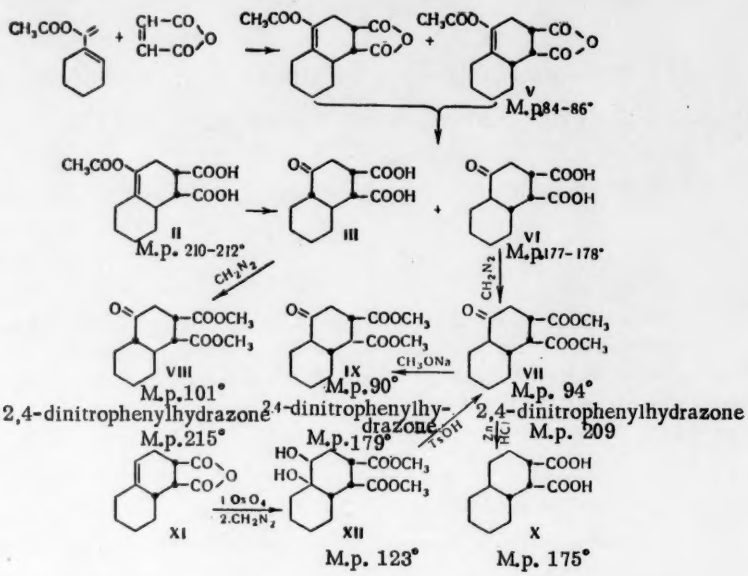
On the basis of these data, it was concluded that the liquid addition product I has an anti-cis-configuration and that diene condensation under these conditions proceeds mainly contrary to the rule of accumulation of unsaturation. A more detailed investigation showed that the liquid addition product I was not a single compound, but that it contained a small amount of the isomeric syn-cis-4-acetoxy anhydride V, which English chemists were recently able to prepare by the condensation of 1-α-acetoxyvinyl-Δ^1-cyclohexene with maleic anhydride at room temperature [2]. It was found that by acid saponification of the crystalline mixture remaining after the separation of the anti-cis-4-acetoxy acid II, it was possible to obtain an 8% yield of the isomeric trans-syn-cis-4-keto acid VI with a m. p. of 177-178°, which was characterized in the form of the crystalline diester VII. This diester is readily isomerized by sodium methylate to the well-known tran-anti-trans-4-keto diester IX [1], and on Clemmensen reduction it gives the previously described trans-syn-cis-decalin-1,2-dicarboxylic acid X [3].

This same trans-syn-cis-4-keto acid VI can also be isolated in 10-15% yield from the products of the acid saponification of the individual anti-cis-4-acetoxy acid II. The latter fact was rather unexpected, and it indicates that either the original anti-cis-4-acetoxy acid II was not pure, or that saponification of the enol acetate group is not stereospecific. Since there apparently was no doubt as to the purity of the anti-cis-4-acetoxy acid II, the second proposal appears probable to us, the more so since certain cases of anomalous isomerization during transformations of cyclic compounds have been described in the literature [4]. If the saponification of the anti-cis-4-acetoxy acid II actually proceeds with the formation of both trans-compounds (III and IV), then, considering the possibility of such an isomerization during the acid hydrolysis of the liquid addition product I, it appears that it can be assumed that the content of the isomeric syn-cis-anhydride did not exceed 5-6%.

The trans-syn-cis-4-keto acid VI and its diester VII prepared by us differed in their constants from the compounds described by the English authors [2]; hence, special proof of the configuration of our compounds

* Deceased

was required. For this purpose, the syn-cis-anhydride XI was oxidized with osmium tetroxide, and after decomposition of the complex and treatment of the hydroxylation product with diazomethane, the cis-glycol ester XII was isolated, the configuration of which corresponded to the addition of the osmium tetroxide from the side opposite to the carboxyl groups [5]. This glycol, owing to the axial location of the tertiary hydroxyl group,



could be readily dehydrated by heating with p-toluenesulfonic acid, giving the trans-syn-4-keto diester VII described above.

Since such a reaction is not directly affected by the asymmetry centers at C_2 C_3 and C_9 and since it leads to trans-linking of the rings, it can be assumed that the keto ester, which is formed as the main reaction product, actually possesses trans-syn-cis-configuration, which is rather unequivocal confirmation of the configurations of the 4-keto acid VI and its diester VII obtained in the diene synthesis.

The fact that the crystalline syn-cis-anhydride V obtained by the English investigators gave hydrolysis products differing from those described by us appears to show that hydrolysis of this anhydride is accompanied by isomerization reactions which prevented these authors from isolating the pure trans-syn-cis-4-keto acid and its diester.

EXPERIMENTAL*

Isolation of the trans-syn-cis-4-ketodecalin-1,2-dicarboxylic acid VI and its diester VII. A mixture of 10 g of the liquid anhydride obtained by condensation of 1-α-acetoxyvinyl-Δ^1-cyclohexene with maleic anhydride in boiling benzene [1] and 45 ml of water was refluxed to complete solution (10-15 minutes). The crystalline product which precipitated during slow cooling (over a period of 3 hours) was filtered and 9 g of the previously described anti-cis-4-acetoxy acid II, m. p. 209-211°, was obtained.

1.2 g of a crystalline product with a m. p. of 150-180° separated on further standing of the mother liquor; this product was refluxed with 6 ml of 0.05% hydrochloric acid, and the resulting solution was concentrated to half its volume. On cooling of the solution, 0.8 g of trans-syn-cis-ketodecalin-1,2-dicarboxylic acid VI separated as the crystal hydrate with a decomposition temperature of 136-139°; after two-fold crystallization from water and drying in air, the compound melted with decomposition at 142-144°.

* All melting points are corrected.

Found %: C 55.84; 55.95; H 6.98; 7.03. $C_{12}H_{16}O_5 \cdot H_2O$. Calculated %: C 55.80; H 7.02.

When the material was dried under vacuum at 80° over calcium chloride, anhydrous trans-syn-cis-4-ketodecalin-1,2-dicarboxylic acid VI with a m. p. of 177-178° was obtained.

Found %: C 59.83; 59.96; H 6.85; 6.72. $C_{12}H_{16}O_5$. Calculated %: C 59.99; H 6.71.

Mol. wt.: found 241.2 (by titration with NaOH), calculated 240.2.

On treatment of the trans-syn-cis-4-keto acid VI with an ethereal solution of diazomethane, the trans-syn-cis-4-keto diester VII was obtained in quantitative yield, and this diester, after crystallization from a mixture of ether and petroleum ether, had a stable m. p. of 93-94° and gave a sharp depression of the m. p. when mixed with the isomeric keto diesters VIII and IX.

Found %: C 62.46; 62.42; H 7.36; 7.47. $C_{14}H_{20}O_5$. Calculated %: C 62.67; H 7.51.

The 2,4-dinitrophenylhydrazone obtained from the trans-syn-syn-4-keto diester VII, after crystallization from a mixture of alcohol and chloroform, melted at 208-209° and gave a depression of the melting point (180-190°) when mixed with the dinitrophenylhydrazone of the isomeric trans-anti-cis-4-keto diester VIII.

Found %: C 53.59; 53.34; H 5.41; 5.45; N 12.67; 1258. $C_{20}H_{24}O_8N_4$. Calculated %: C 53.52; H 5.39; N 12.49.

Saponification of anti-cis-4-acetoxy-Δ^4-octalin-1,2-dicarboxylic acid II. A mixture of 8 g of anti-cis-4-acetoxydicarboxylic acid II with a m. p. of 210-212°, 50 ml of water, and 10 ml of 3% hydrochloric acid war refluxed for 15 minutes, after which the solution was concentrated to one-third of its original volume. On standing of the solution, 6.8 g of a mixture of the monohydrates of the isomeric keto acids III and VI with a m. p. of 108-115° separated. Crystallization of this mixture from 32 ml of water gave 4.6 g of a substance with a m. p. of 115-118°, and a second recrystallization from water gave 3.7 g of the pure crystal hydrate of the trans-anti-cis-4-keto acid III with a decomposition temperature of 121-123°; a mixture with the previously described compound [1] showed no m. p. depression.

The mother liquor from the first recrystallization was allowed to stand for two days, after which 2 g of a crystalline product with a m. p. of 122-129° was recovered. After three-fold crystallization of this product from water, 1 g of the trans-syn-cis-4-keto acid was obtained in the form of the monohydrate with a m. p. of 142-144°; drying of this product under vacuum gave pure trans-syn-cis-4-ketodecalin-1,2-dicarboxylic acid VI with a m. p. of 176-177°, which did not give a m. p. depression with the sample described above.

Preparation of the cis-glycol XII and its dehydration. To a solution of 3 g of the syn-cis-anhydride XI in 200 ml of absolute ether was added 4 g of osmium tetroxide, and the mixture was allowed to stand at room temperature for 5 days. The either was distilled, the residue was dissolved in 200 ml of alcohol, a solution of 28 g of sodium sulfite in 150 ml of water was added, and the mixture was refluxed for 4 hours. The precipitate was filtered, the mother liquor was concentrated to a volume of 25-30 ml, and the crystalline hydroxylation product was filtered and treated with an excess of an ethereal solution of diazomethane. After distillation of the ether, 3.2 g of the cis-glycol ester XII was obtained, which, after crystallization from a mixture of ether and methanol (5:1), had a stable m. p. of 122-123°.

Found %: C 58.76; 58.60; H 7.78; 7.71. $C_{14}H_{22}O_6$. Calculated %: C 58.73; H 7.74.

For dehydration, a mixture of 1.4 g of cis-glycol XII and 0.1 g of p-toluenesulfonic acid was heated for 10 minutes at 120-130° under a vacuum of 100 mm. The reaction product was extracted with ether, and the ethereal solution was washed with water, dried with sodium sulfate, and the ether distilled. The liquid residue gradually crystallized on standing with dilute hydrochloric acid (1:1). 0.9 g of the trans-syn-cis-4-keto diester VII was obtained, and this, after crystallization from a mixture of ether and petroleum ether, melted at 92-94° and did not give a m. p. depression when mixed with the sample obtained above.

On reduction of the keto diester VII by the Clemmenson method, there was obtained a good yield of the trans-syn-cis-acid X with a m. p. of 173-175° [3].

Summary. It was shown that the liquid addition product formed by the condensation of 1-α-acetoxyvinyl-Δ^1-cyclohexene with maleic anhydride in boiling benzene contains chiefly the anti-cis-4-acetoxy anhydride I and a small amount (5-6%) of the isomeric syn-cis-adduct V. The presence of this isomer, which is formed as a result of a reaction proceeding in conformity with the principle of Alder, was shown by the preparation of the corresponding trans-syn-4-keto acid VI and the diester VII, the configuration of which was demonstrated by dehydration of the cis-glycol XII.

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR

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REACTIONS OF FERROCENESULFONIC ACIDS

Academician A. N. Nesmeianov, E. G. Perevalova, S. S. Churanov and O. A. Nesmeianova

In a previous communication [1], we described the sulfonation of ferrocene with various sulfonating agents and some derivatives of ferrocenesulfonic acids. In the present work, a number of other sulfur-containing derivatives of ferrocene was prepared, and an attempt was made to carry out exchange reactions of the sulfonyl group.

By the reaction of the lead salt of ferrocenedisulfonic acid, $Fe(C_5H_4SO_3)_2Pb \cdot 4H_2O$, with phosphorus trichloride, we obtained the monoacyl chloride, $ClSO_2C_5H_4FeC_5H_4SO_3H$.

Phosphorus oxychloride reacts with the lead salt of the disulfonic acid to form the dichloride of ferrocenedisulfonic acid, and it oxidizes the lead salt of the monosulfonic acid to the ferricinium cation; the latter reaction is accompanied by the appearance of an intense dark green color, and the reaction can be used as a qualitative test to distinguish these acids.

We were unable to prepare the acid chlorides of either the mono- or the disulfonic acid from the barium salts.

By heating ferrocenedisulfonyl chloride with diethylamine, we obtained the bis(diethylamide) of ferrocenedisulfonic acid, $Fe[C_5H_4SO_2N(C_2H_5)_2]_2$.

From ferrocenemonosulfonyl chloride• was prepared the diethylamide,•• the sodium salt of the sulfinic acid, ferrocenyl disulfide, and ferrocenthiol, which was isolated in the form of derivatives – the benzoate and S-ferrocenylthioglycolic acid. In air, the ferrocenethiol rapidly changed to the disulfide. When heated with $HgCl_2$, the sodium salt of the sulfinic acid was smoothly converted to ferrocenylmercury chloride.

On reduction, the ferrocenedisulfonyl chloride gave a halogen-free substance, probably a disulfide polymer, which was not isolated in the pure form.

In the infrared spectra of all of the mono-substituted sulfur compounds of ferrocene prepared by us there were characteristic maxima in the 1000 and 1110 cm^{-1} regions, indicating [3, 4] the presence of a free cyclopentadienyl ring. These maxima were absent from the spectra of all of the disubstituted sulfur derivatives of ferrocene, which confirms our previous proposal [1] that the sulfonyl groups are located on different cyclopentadienyl rings.

Our attempts to replace the sulfonyl group by hydroxyl by means of alkali fusion, by a cyano group through the action of potassium ferricyanide, and by a formyl group by heating with sodium formate were unsuccessful and led to complete destruction of the ferrocene nucleus with the formation of iron salts or the hydroxide.

We were also unable to carry out the hydrolysis of the sulfonic acids with the formation of ferrocene. In the case of the monosulfonic acid, long heating in strongly acid solution resulted in oxidation to a derivative

•The preparation of ferrocenemonosulfonyl chloride was described in a previous communication [1].

••The diethylamide of ferrocenemonsulfonic acid was prepared by N. A. Nesmeianov.

of the ferricinium cation and subsequent decomposition. In the case of the disulfonic acid, decomposition of part of the acid occurred during the mere evaporation of solutions of the free acid or of its salts. When an aqueous solution of the disulfonic acid was heated in a sealed tube for 6 hours, more than 25% of the acid decomposed, as shown by a quantitative determination of ionic iron. Evidently, the stability of the bond between the iron and the cyclopentadienyl ring is considerably decreased in comparison with ferrocene by the presence of the sulfonyl groups.

The introduction of a sulfonyl group sharply decreases the tendency toward further substitution in the same cyclopentadienyl ring and, to a considerably lesser extent, in the other ring. This is indicated by the formation of ferrocenemonosulfonic acid in good yield and practically no disulfonic acid during the sulfonation of ferrocene [1]. The considerable passivation of the ferrocene nucleus with respect to further electrophilic substitution also indicates that it will not be possible to prepare the trisulfonic acid.

The effect of the sulfonyl group on the reactivity of the ferrocene nucleus is similar to that of the acetyl group [5].

EXPERIMENTAL

Preparation of ferrocenedisulfonyl chloride. 12 g of the lead salt of ferrocenedisulfonic acid (contained $4H_2O$) and 30 ml of $POCl_3$ were heated for 40 minutes, and the reaction mixture was then poured onto ice; the precipitate was filtered and extracted with dichloroethane (200 ml) in a Soxhlet extractor. The dichloroethane was distilled to incipient crystallization. The remaining solution was cooled to 0 deg, and the precipitated crystals of ferrocenedisulfonyl chloride were filtered (weight 4.2 g). Another 0.8 g of the chloride was recovered from the mother liquor. The total yield was 5 g (64% of theoretical).

The dichloride was recrystallized from a mixture of dichloroethane and CCl_4 (1:1). It was a yellow-orange crystalline material, readily soluble in dichloroethane and benzene and slightly soluble in ether. The dichloride decomposed explosively when heated above 150°, and it darkened above 135° when heated in a sealed tube.

Found %: C 31.87; 31.84; H 2.30, 2.29. $C_{10}H_8O_4S_2Cl_2Fe$. Calculated %: C 31.35; H 2.10.

Preparation of the monochloride of ferrocenedisulfonic acid. 2.9 g of the lead salt of ferrocenedisulfonic acid was added, with stirring, to 20 ml of PCl_3. The mixture was refluxed for 1 hour. The resulting yellow solution was filtered. The filtrate was heated with 10 ml of PCl_3 and 20 ml of dichloroethane. The insoluble material was again filtered and washed with dichloroethane. The major part of the solvent and PCl_3 was distilled under vacuum, and the residue was evaporated in a vacuum desiccator over sodium hydroxide. The precipitated monosulfonyl chloride was washed with methyl alcohol and dried in a vacuum desiccator. The yield was 0.65 g (36% of theoretical).

The monochloride of ferrocenedisulfonic acid is a yellow powdery material which decomposes on heating above 129°, and which is difficultly soluble in water.

Found %: C 33.60, 33.55; H 2.44, 2.44; Fe 15.25, 15.50. $C_{10}H_9O_5S_2ClFe$. Calculated %: C 32.99; H 2.49; Fe 15.32.

Qualitative differentiation of ferrocenesulfonic acids. 0.1-0.2 g of the lead salt of the ferrocenesulfonic acid is heated to boiling with 5 ml of PCl_3; the mixture is held at this temperature for 3-5 minutes, and is then poured onto ice. The formation of a red precipitate of acid chloride after hydrolysis of all of the PCl_3 is characteristic of the monosulfonic acid. The lead salt of ferrocenedisulfonic acid gives a yellow solution.

If $POCl_3$ is used, a precipitate is formed in the case of the lead salt of the disulfonic acid, while the monosulfonic acid forms a green solution.

Preparation of the bis(diethylamide) of ferrocenedisulfonic acid. 1 g of ferrocenedisulfonyl chloride and 50 ml of diethylamine were heated at the boiling point for 6 hours. The mixture was cooled, and the precipitated crystals of the bis(diethylamide) were filtered. The weight was 0.4 g. Dilution of the diethylamine solution with water gave an additional 0.7 g of material.

The bis(diethylamide) of ferrocenedisulfonic acid was recrystallized from ethyl acetate to which a few drops of ethyl alcohol were added. It was a golden yellow crystalline material, readily soluble in organic in solvents. M. p. 159-161°. The yield was 92% of theoretical.

Found %: C 47.84, 47.87; H 6.28, 6.34; Fe 12.37, 12.41. $C_{18}H_{28}O_4N_2S_2Fe$. Calculated %: C 47.36; H 6.18; Fe 12.23.

Preparation of the diethylamide of ferrocenemonosulfonic acid. This substance was prepared in a manner similar to that of the preceding example (heated for 3 hours). The yield was almost quantitative. The diethylamide of ferrocenemonosulfonic acid was a light yellow crystalline material, readily soluble in organic solvents and crystallizable from methyl alcohol and carbon tetrachloride. M. p. 91-92°.

Found %: C 52.25, 52.33; H 6.09, 6.20; S 10.06, 9.71; Fe 17.61, 17.49. $C_{14}H_{19}O_2NSFe$. Calculated %: C 52.37; H 5.96; S 9.97; Fe 17.40.

Reduction of ferrocenemonosulfonylchloride.

A. Sodium salt of the sulfinic acid. A mixture of 5 g of ferrocenesulfonyl chloride, 10 g of Zn dust, 150 ml of ether, and approximately 0.5 ml of water was refluxed for 1 hour. The precipitate was filtered and heated for 10 minutes with a saturated soda solution. The solution was filtered hot, and then cooled to precipitate the Na salt of the sulfinic acid (2 g), which was recrystallized from alcohol (contained $2H_2O$).

Found %: C 39.09, 39;38; H 4.20, 4.26. $C_{10}H_{13}SO_4FeNa$. Calculated %: C 38.98; H 4.25.

B. S-Ferrocenylthioglycolic acid. A solution of 5 g of ferrocenesulfonyl chloride in absolute ether was gradually added to an excess of an ethereal solution of $LiAlH_4$. The mixture was heated 1 hour, and was then poured into 200 ml of ice water acidified with 5 ml of concentrated HCl. The ethereal solution, which contained ferrocenethiol, was separated, washed twice with water, and extracted with 10 ml of 20% NaOH. To the resulting aqueous solution of sodium ferrocenethiolate was added an excess of a saturated solution of monochloroacetic acid in 20% NaOH. After 30 minutes, the mixture was acidified and extracted with ether. The ether was evaporated, and the S-ferrocenylthioglycolic acid which remained was recrystallized from aqueous alcohol. M. p. 109-110. The yield was 2.7 g (56% of theoretical).

Found %: C 52.39, 52.23; H 4.45, 4.39; S 11.12, 11.03; Fe 20.06, 20.00. $C_{12}H_{12}SO_2Fe$. Calculated %: C 52.19; H 4.38; S 11.60; Fe 20.20.

In addition, 0.9 g of ferrocenyl disulfide was also isolated.

C. Ferrocenyl disulfide. On distillation of the ether from a solution of ferrocenethiol, prepared as described in Experiment B, ferrocenyl disulfide separated in good yield; this substance was identical with that previously synthesized by us from diferrocenylmercury [2].

D. Thioferrocenyl benzoate [ferrocenyl thiolbenzoate]. 0.98 g of ferrocenyl disulfide was heated for 1 hour with an excess of an ethereal solution of $LiAlH_4$. Further treatment of the reaction mixture was as described in Experiment B. Then, benzoyl chloride was gradually added, with vigorous stirring, to the solution of ferrocenethiol in 10% NaOH until the solution was almost completely decolorized. The precipitated thioferrocenyl benzoate [ferrocenyl thiolbenzoate] was extracted with ether, and, after distillation of the ether, it was recrystallized from butyl alcohol. M. p. 138-139°. The yield was 1.33 g (92% of theoretical).

Found %: C 62.91, 62.64; H 4.36, 4.33; Fe 17.45, 17.42. $C_{17}H_{14}SOFe$. Calculated %: C 63.36; H 4.38; Fe 17.30.

Hydrolysis of ferrocenedisulfonic acid. 2.0696 g of ferrocenedisulfonic acid (contained $4H_2O$; m. p. 123-125° in a sealed capillary* was dissolved in 25 ml of water and heated in a sealed tube at 100° for 6 hours. The solution was diluted with water (ferrocene did not precipitate), and the ionic iron was precipitated with ammonia. The weight of ferric oxide after calcination was 0.1051 g. Consequently, 26% of the original sulfonic acid had decomposed.

Ferrocenedisulfonic acid does not contain ionic iron, and a precipitate does not form on treatment with ammonia.

Infrared spectra of sulfur compounds of ferrocene. The infrared spectra were taken with an IKS-11 single-

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* In our previous communication [1], we gave a m.p. of 80-90° for ferrocenedisulfonic acid, which value applies to samples in air; in the same article, we neglected to give the m.p. of ferrocenemonosulfonic acid (117-118° in a sealed capillary).

beam spectrometer, and the spectra were recorded with an EPP-09 recorder in the narrow region from 970 to 1250 cm^{-1}; sodium chloride prism and cells were used. The substances were used in the form of suspensions in vaseline oil.*

Ferrocenemonosulfonic acid: 1000; 1018; 1065; 1107; 1166; 1172. Lead salt of ferrocenemonosulfonic acid: 1011; 1047; 1109; 1125; 1137; 1224. Methyl ester of ferrocenemonosulfonic acid: 1004; 1018; 1030; 1106; 1149; 1176; 1200. Ferrocenemonosulfonyl chloride; 999; 1017; 1032; 1110; 1140; 1180; 1202.

Ferrocenedisulfonic acid: 832; 1013; 1049; 1092; 1129; 1157; 1223; 1228. Lead salt of ferrocenedisulfonic acid: 1009; 1043; 1059; 1153. Dimethyl ester of ferrocenedisulfonic acid: 985; 1021; 1035; 1151; 1182; 1202.

Ferrocenedisulfonyl chloride: 1023; 1035; 1146; 1176; 1202.

Monochloride of ferrocenedisulfonic acid: 1013; 1022; 1037; 1083; 1149 cm^{-1}.

M. V. Lomonosov Moscow State University

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*The authors wish to acknowledge their indebtedness to L. A. Kazitsyna and B. V. Lokshin for aid in taking the spectra.

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THE NATURE OF THE WATER IN HETEROPOLY COMPOUNDS OF TUNGSTEN HETEROPOLY ACIDS

E. Ia. Rode

(Presented by Academician I. L. Cherniaev, October 5, 1957)

According to the major hypotheses on the structure of heteropoly acids, their general formula can be represented as $H_{12-m}[R(Me_2O_7)_6] \cdot H_2O$ (according to Miolati-Rosenheim [1, 2]) or $H_{8-m}[R(Me_3O_{10})_4] \cdot nH_2O$ (according to x-ray structural data [3]), where R is the complex-forming element (phosphorus, silicon, boron, etc.), Me is a metal (tungsten, molybdenum, etc.), m is the valence of the complex former, and n represents the number of molecules of water of crystallization. In agreement with these formulas, the basicity must differ among heteropoly acids (12 − m and 8 − m). The amount of water of crystallization in heteropoly acids synthesized by crystallization from aqueous solutions must vary depending on the conditions used. According to Kraus [4], six series of crystallochemically different hydrates are formed.

On the basis of a study of the dehydration processes of certain aquopoly compounds [5] and, subsequently, of heteropoly compounds [6], it has been proposed that a part of the water molecules plays a special role in these compounds. However, as the net result of investigations of the bond strength of water in certain aquopoly compounds, by means of the stable isotopes of hydrogen and oxygen-deuterium and O^{18} – Vikt. I. Spitsyn and coworkers [7] were unable to establish a difference in the nature of water bonds or to establish the existence of "special" water molecules in these compounds.

West and Audrieth [8] found that on the differential thermograms of preparations of phospho- and silicotungstic and phospho- and silicomolybdic acids dried over sulfuric acid, there are two thermal effects corresponding, in the opinion of the authors, to: first (endothermic), the removal of zeolitic water and, second (exothermic), the decomposition of the heteropoly compound.

E. A. Nikitina and E. V. Buris [9], as a result of a thermographic investigation of these same acids, came to the conclusion that their basicities corresponded to those which coordination theory predicts for them.

We carried out a study of a series of heteropoly acids of tungsten and molybdenum and their salts using various methods of physicochemical analysis. The results obtained are of particular interest for forming an opinion as to the role of the physicochemical nature of the water in these compounds. In the present article, we present some data obtained with the cooperation of N. A. Kotorov during an investigation of phosphotungstic and silicotungstic heteropoly acids. These acids were synthesized by well-known methods [10].

The compounds investigated have typical differential thermograms and thermogravimetric dehydration pyrolysis curves (curves of water content vs. temperature), which were obtained simultaneously with the thermograms. A comparison of the endothermic effects observed on the thermograms of preparations of different degrees of hydration with the corresponding stage of hydration on the corresponding pyrolysis curves permits specific conclusions both as to the nature of the processes occurring during heating and as to the physicochemical nature of the products formed.

We studied preparations of phosphotungstic acid of different degrees of hydration. Curve I in Figure 1 is the thermogram for a preparation of this acid having a total water content, x, calculated on the basis of a molecule of $P_2O_5 \cdot 24WO_3$ residue, of 31.4 moles (n = 14.2). The preparation was obtained by partial dehydration over sulfuric acid of a highly hydrated sample (x = 61.0 moles), which was crystallized at room temperature.

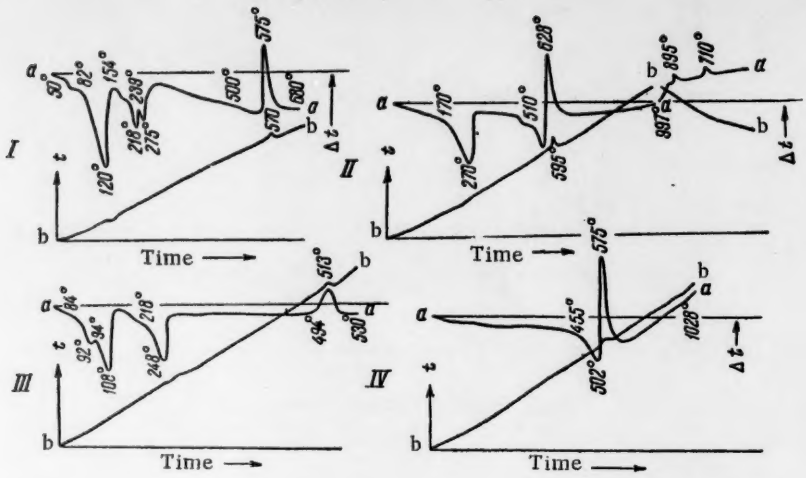

Fig. 1. Thermograms of samples of heteropoly acids of differing degrees of hydration: I – phosphotungstic acid, x = 31.4 H_2O; II – the same, x = 5.0 H_2O; III – silicotungstic acid, x = 18.6 H_2O; IV – the same, x = 2.0 H_2O.

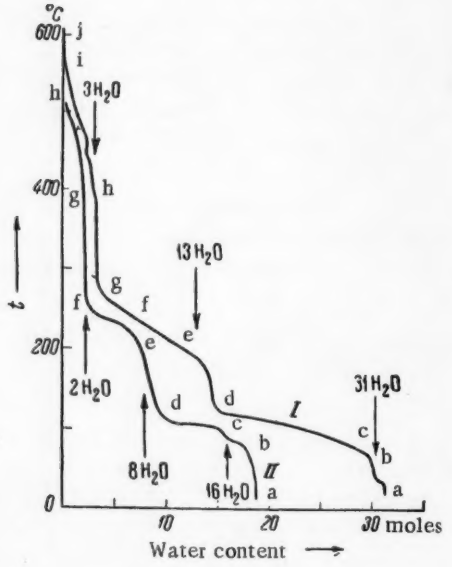

Fig. 2. Dehydration pyrolysis curves (composition-temperature curves) of the samples; I – phosphotungstic acid, x = 31.4 H_2O; II – silicotungstic acid, x = 18.6 H_2O.

Curve I in Figure 2 is a pyrolysis curve showing the water content, x, calculated as the per cent water loss during heating.

On pyrolysis curve I (Figure 2) there are two clearly expressed, almost vertical portions b – c and g – h at ordinates of x = 31H_2O and 3H_2O, respectively, and a sloping portion d – e in the region of x = 16H_2O to 13H_2O. The ordinates x = 31H_2O and 13H_2O correspond, as shown by calculation, to the previously studied compounds $H_3[P(W_3O_{10})_4] \cdot nH_2O$ with n = 14 (triclinic hydrate) and n = 5 (cubic hydrate) [4]. The ordinate x = 3H_2O (n = 0) corresponds to the compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$, or anhydrous phosphotungstic acid $H_3[P(W_3O_{10})_4]$.

The three clearly expressed endothermic effects observed on thermogram I of Fig. 1 after a small effect at 50°, due to the elimination of water above the composition 31.0 H_2O, correspond to: first, at 82-120° corresponding to the portion c – d of pyrolysis curve I in Figure 2, the decomposition of the hydrate x = 31.0 H_2O with the formation of a phase of variable composition having a limiting composition corresponding to point d (x = 15.6H_2O); second, at 154-218° corresponding to the portion d – e of the pyrolysis curve, the decomposition of this phase with the formation of the hydrate x = 13.0H_2O; third, at 239-275° corresponding to the portion e – f – g of the pyrolysis curve, the decomposition of the latter hydrate with the formation, at first, of a phase of variable composition corresponding to point f (x ≃ 7) and then decomposing further with the formation of the compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$. This compound is stable to heating up to 400° (vertical portion g – h). On further heating, it decomposes with the elimination of 3 molecules of water, giving a fourth diffuse endothermic effect at 500-570°, which is located immediately before the next, exothermic, effect at 570-575°.

The endothermic effect corresponding to decomposition of the indicated compound at 510-595° appears clearly on thermogram II of Figure 1 for the preparation $5.0 \cdot H_2O \cdot P_2O_5 \cdot 24WO_3$ (phase of variable composition), which was obtained by prolonged heating of the original sample at 150°. The endothermic effect at 170-270° on the latter thermogram corresponds to the decomposition of the indicated phase with the formation of the compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$. As the x-ray investigation showed, the amorphous trioxide WO_3, liberated during the decomposition of this compound, then crystallizes, producing the exothermic effect at 595-628° which is analogous to the effect on thermogram I.

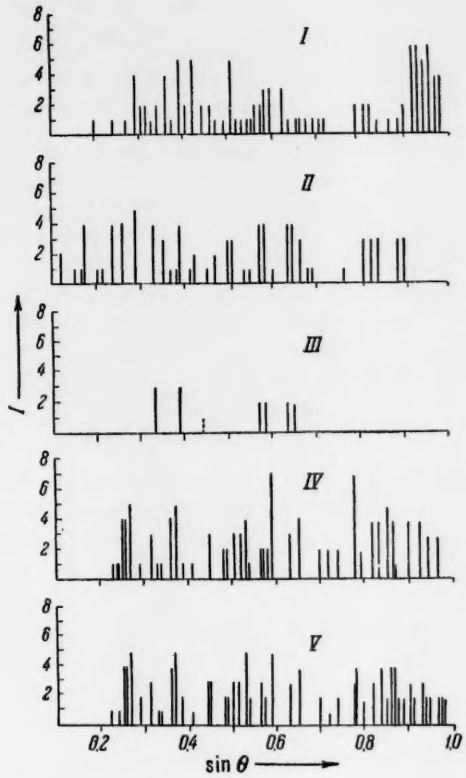

Fig. 3. Graphs of the intensities, $\underline{I}$, of the diffraction lines on x-ray powder patterns of preparations of phosphotungstic acid heated at various temperatures. Explanation in the text (I is the original preparation).

In Figure 3 is presented a graph (II) of the intensities of the diffractions lines on the x-ray pattern of the indicated compound, which was prepared by heating the original sample at 250° (the patterns were taken with iron radiation). Heating at 450° (Graph III, Figure 3), i. e., in the region of decomposition of this compound, led to almost complete decomposition and amorphization of the preparation (only six lines remained). Further heating at a higher temperature led to the appearance of well-defined lines of the trioxide WO_3 (Graph IV for the preparation heated at 630°), as is shown by a comparison with Graph V for the pure trioxide heated at this same temperature of 630°. On cooling curve II of Figure 1 there are two exothermic effects at 895 and 710°, which correspond to polymorphic transformations of WO_3.

We also studied preparations of silicotungstic acid of differing degrees of hydration.

Similarly to the preceding, a comparison of the endothermic effects on pyrolysis curve III of Figure 1 for a preparation of this acid (containing 8.6 moles of water) with the stages on the corresponding pyrolysis curve II in Figure 2 indicates the formation of hydrates with $x = 16H_2O$ and $8H_2O$ and of the compound $2H_2O \cdot SiO_2 \cdot 12WO_3$, which corresponds in composition to anhydrous silicotungstic acid $H_4[Si(W_3O_{10})_4]$ (vertical part f – g of the pyrolysis curve).

Here, too, the amorphous trioxide WO_3, which is formed as one of the decomposition products, crystallizes, producing exothermic effects on thermograms III and IV (at 494-513° and 502-575°). The formation, during the process of heating the acids, of the above-mentioned hydrates of constant and variable composition is confirmed by a study of the composition-temperature diagrams, which were obtained under equilibrium conditions. Recalculation of the compositions of the hydrates of constant composition to the x-ray structural formulas $H_3[P(W_3O_{10})_4] \cdot nH_2O$ and $H_4[Si(W_3O_{10})_4] \cdot nH_2O$ gives the following values for the coefficient n: 14 and 5 for phosphotungstic acid and 14 and 6 for silicotungstic acid. With the first acid, there was also observed the formation of phases of variable composition in the ranges of n of 6.3 to 5 and 2.1 to 0.

With respect to its physicochemical nature, the water in these hydrates is water of crystallization. It is removed completely by heating to 250°. This process is reversible, and does not lead to decomposition of the heteropoly acid.

Of particular interest is the formation, during thermal decomposition, of the compounds $3H_2O \cdot P_2O_5 \cdot 24WO_3$ and $2H_2O \cdot SiO_2 \cdot 12WO_3$, which correspond in composition to the anhydrous acids $H_3[P(W_3O_{10})_4]$ and $H_4[Si(W_3O_{10})_4]$. According to its physicochemical nature, the water evolved during heating of these compounds differs from water of crystallization, and must be a type of more strongly bound water of constitution. It is apparently formed from hydrogen or oxonium ions [4, 11] as a result of irreversible decomposition of the substance. The amount of this water corresponds to that required for the presence in a special position in the structure of three (in the case of phosphotungstic acid) and four (in the case of silicotungstic acid) hydrogen atoms per atom of complex former. The number of such atoms agrees with the basicity of these acids as determined from x-ray structure theory. The decomposition of the indicated compounds is exothermic as shown by the thermographic investigation, and not endothermic, as assumed by West and Audrieth [8].

As proposed by E. A. Nikitina and E. V. Buris [9], the formation, during thermal decomposition, of heteropoly acid compounds corresponding in composition to the Miolati-Rosenheim formula does not occur; the dehydration pyrolysis curves show no steps corresponding to such compounds, and there are no effects on the thermograms which would correspond to their formation or decomposition.

N. S. Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences USSR

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POLYMERIZATION OF ISOBUTYLENE UNDER THE INFLUENCE OF BORON TRIFLUORIDE ON ALUMINUM OXIDE

Academician A. V. Topchiev and L. A. Aliavdina

The present article contains the results of an investigation of the effect of temperature, space rate, catalyst support, and catalyst age on the polymerization of isobutylene in the presence of boron trifluoride adsorbed on aluminum oxide. The experiments were carried out at atmospheric pressure.

The isobutylene was obtained by the dehydration of isobutyl alcohol (b. p. 107°) over aluminum oxide at 400°. Analysis showed that the resulting gas contained 97-98% isobutylene. The boron trifluoride was prepared by the method described in references [1, 5].

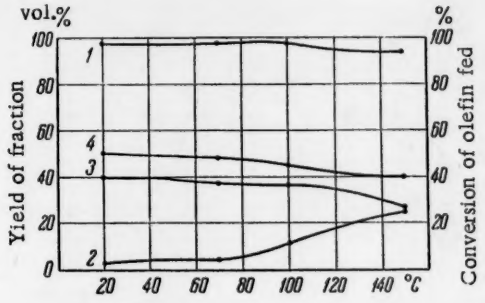

Fig. 1. Effect of temperature on isobutylene conversion (1) and on the yield of various polymer fractions at a space rate of 60 hours^{-1} with a catalyst of BF_3 on aluminum oxide. 2 – 98-126° fraction, 3 – 170-185° fraction, 4 – fraction boiling above 185°.

The experiments (without BF_3 in the feed) were carried out at space rates of 60 and 300 hours^{-1} and at temperatures of 20, 70, 100, and 150°. The aluminum oxide was dried at 250° for 3 hours, after which boron trifluoride was adsorbed on it at 150°. The samples were brought to constant weight.

50 liters of isobutylene and 68 g, or 100 cc, of aluminum oxide containing 20-21 g of adsorbed boron trifluoride (29-31%) were used in each experiment. The boron trifluoride-aluminum oxide catalyst was charged to a reactor 40 cm long and 2.6 cm in diameter, into which the isobutylene was passed from a gasometer. To the effluent end of the reactor was joined a tube filled with pieces of NaOH to remove boron trifluoride. The reactor was fitted with an electric heater. In the experiments at 20°, water was used to cool the reactor. The polymer was washed, dried, and distilled in a column.

As seen from Figure 1, at a space rate of 60 hours^{-1} and temperatures of 20, 70, 100, and 150°, the conversion of isobutylene was 94-98%. With an increase in temperature, the yield of the fraction above 185° decreased from 51 to 40%, the fraction boiling from 170-185° decreased from 40 to 27%, and the yield of the fraction boiling at 98-126° increased from 3.2 to 25.6%.

Thus, the degree of isobutylene polymerization decreased with increasing temperature, as may also be seen from Table 1 in which are reported the physicochemical constants of the polymer and the experimental conditions.

In Table 1 are reported the results of an investigation of two polymers obtained at 150° and space rates of 300 and 60 hours^{-1} (without BF_3 in the feed). The polymer was heavier in the latter experiment. Consequently, isobutylene polymerization becomes deeper as time of contact with the boron trifluoride is increased, or space rate is decreased.

The polymerization of isobutylene was also studied at 150° with boron trifluoride in the feed; the molecular compound $K_2SO_4 \cdot BF_3$ served as the source of boron trifluoride. The compound $K_2SO_4 \cdot BF_3$, which we were the first to use for the polymerization of isobutylene [2], was prepared [3, 4] by the reaction of dry boron trifluoride with calcined K_2SO_4 at 235°. The samples were brought to constant weight.

TABLE 1

Type of experiment	Am't of isobutylene, liters	Space rate, hours^{-1}	Conversion %	Temp., °C	Am't of BF_3, g	d_4^{20}	n_D^{20}	Initial b.p. °C	Frac. from i.b.p. to 106°, vol.%	Frac. 106-126° vol. %
Without BF_3 in feed	50	60	98	20	20.5	0.7915	1.4479	105	0.8	2.4
	50	60	98	70	20	0.7745	1.4387	101	1.2	4
	50	60	98	100	21	0.7638	1.4340	99	6.4	5.2
	50	60	94	150	21	0.7560	1.4294	75	14.4	11.2
	50	300	84	150	20	0.7339	1.4197	72	26	9.6
With BF_3 in feed	50	60	65	150	5	0.7190	1.4132	67	48.9	16
	50	60	70	150	20	0.7216	1.4135	72	36	23.4
	250	60	67	150	5	0.7168	1.4126	67	49.2	14.8

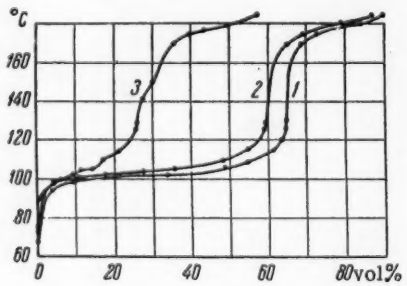

Fig. 2. Fractional composition of isobutylene polymer obtained with BF_3 – aluminum oxide catalyst at 150° and a space rate of 60 hours^{-1} with BF_3, from $K_2SO_4 \cdot BF_3$, in the feed (1 – 5 g, 2 – 20 g) and without BF_3 in the feed (3 – 20 g).

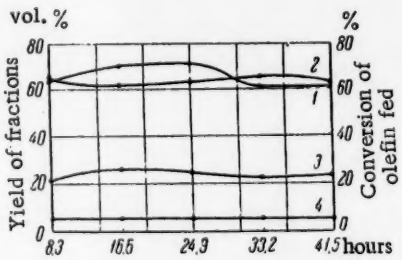

Fig. 3. Effect of catalyst age on the conversion of isobutylene (1) and on the yield of various polymer fractions; catalyst, BF_3 on aluminum oxide; 150°; space rate, 60 hours^{-1}. 2 – 67-126° fraction, 3 – 170-185° fraction, 4 – fraction above 185°.

In the experiments in which boron trifluoride from $K_2SO_4 \cdot BF_3$ was included in the feed, 68 g (100 cc) of dry aluminum oxide was placed in the reactor. Then 5 or 20 g of boron trifluoride and 50 liters of isobutylene from the gasometer were simultaneously fed to the reactor; the isobutylene space rate was 60 hours^{-1} (see Table 1). The boron trifluoride was obtained by the decomposition of, respectively, 17.8 and 71.2 g of $K_2SO_4 \cdot BF_3$ at 360-390°.

The physicochemical constants of the resulting polymer were: d_4^{20} 0.7190, n_D^{20} 1.4132, mol. wt. 119.7, bromine number 132, unsaturates 98.7%, octane number 87. The molecular weight was determined cryoscopically; the octane number was determined by the motor method using a "Vokesh" apparatus.

In Figure 2 are presented fractional distillation curves for three polymers obtained at 150 ° both with and without boron trifluoride, from $K_2SO_4 \cdot BF_3$, in the feed. The polymers obtained with 5 and 20 g of boron trifluoride in the feed were considerably lighter than the polymer obtained with 20 g of boron trifluoride but without boron trifluoride in the feed (cf. Table 1).

From the above material it follows that with a feed containing boron trifluoride from the molecular compound $K_2SO_4 \cdot BF_3$, the degree of polymerization of isobutylene is decreased.

All of the polymers obtained at 150° contained 6-13% of the 72-100° fraction, the presence of which is explained by cracking due to the aluminum oxide carrier.

The life of the boron trifluoride-aluminum oxide catalyst was studied at 150° with a feed containing boron trifluoride from the molecular compound $K_2SO_4 \cdot BF_3$.

68 g of aluminum oxide, 17.8 g of $K_2SO_4 \cdot BF_3$ containing 5 g of boron trifluoride, and 250 liters of isobutylene were used in the experiment, which continued for 41.5 hours (see Table 1).

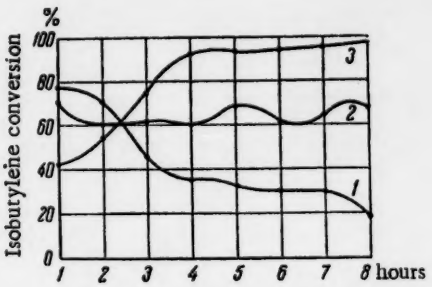

Fig. 4. Effect of the carrier on isobutylene conversion during polymerization with BF_3 catalyst at 150° and a space rate of 60 $hours^{-1}$. 1 – BF_3, 2 – aluminum oxide and BF_3, 3 – activated charcoal and BF_3.

It is seen from Figure 3 that the resulting polymer was very light, since it contained 62.5-65.6% of the fraction boiling at 67-126° and only 5% of the fraction boiling above 185°. The average isobutylene conversion was 67%. The octane numbers of the 98-106 and 170-185° fractions were, respectively, 100 and 90. The physicochemical constants of the polymer were: d_4^{20} 0.7168, n_D^{20} 1.4126, bromine number 136, molecular weight 116, unsaturates 98.6%, octane number 87.

The investigation showed that the catalyst remains active and effective for a long time at 150° without regeneration. The resulting isobutylene polymer can be used as a component of motor fuel, as was remarked in the work with silica gel [1].

In Table 2 is presented the chemical composition of certain fractions of the polymer; the composition was determined by means of Raman analysis.

TABLE 2

Catalyst	Expt. temp. ° C	Space rate, $hours^{-1}$	B.p. of frac., ° C	d_4^{20}	n_D^{20}	Chemical composition	B.p. from [6] ° C
BF_3 on aluminum oxide	150	60	98–106	0.7180	1.4117	2,4,4-Trimethyl-1-pentene	101.36
						2,4,4-Trimethyl-2-pentene	104.85
Same	150	60	108–120	0.7350	1.4222	3,4,4-Trimethyl-2-pentene	112.3
						2,3,4-Trimethyl-2-pentene	116.26
						2,3,4-Trimethyl-1-pentene	117.15

As seen from Table 2, the polymerization of isobutylene is accompanied by isomerization reactions, owing to which 3,4,4-trimethyl-2-pentene is formed, and then 2,3,4-trimethyl-2-pentene and 2,3,4-trimethyl-1-pentene. In the experiments at 150°, the 108-126° fraction was 16-23% of the polymer (see Table 1).

In the experiments on the effect of the carrier, 68 g of aluminum oxide dried at 250° or 20 g (100 cc) of wood charcoal dehydrated under vacuum at 300° was used. In each experiment at 150°, 5 g of boron trifluoride, obtained by the decomposition of 17.8 g of $K_2SO_4 \cdot BF_3$, and 50 liters of isobutylene were simultaneously fed to the reactor; the isobutylene feed rate was 6 liters/hour.

As seen from Figure 4, with no carrier present the isobutylene conversion dropped with time, reaching a value of 18.7%; in the experiments with a carrier, the conversion either increased to 96% (with activated charcoal) or remained constant at 61-71% (with aluminum oxide).

Thus, it is expedient to use a carrier such as activated charcoal or aluminum oxide in the polymerization of isobutylene with boron trifluoride.

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SYNTHESIS OF SILICOORGANIC COMPOUNDS CONTAINING METHACRYLYL GROUPS

K. A. Andrianov and A. K. Dabagova

(Correspondent Member Academy of Sciences USSR)

As a development of the investigations carried out previously [1], in this report we describe the preparation of new silicoorganic compounds, containing a methacrylyl group in the hydrocarbon radical at the silicon atom, methacryloxymethylalkoxysilanes and methacrylyl compounds of tri-, tetra- and pentasiloxanes. The methacryloxymethylalkoxysilanes were prepared by the scheme:

$$ClCH_2Si(OR)_{3-n} + CH_2=C(CH_3)COOK \xrightarrow{-KCl} CH_2=C(CH_3)COOCH_2Si(OR)_{3-n}$$
$$\quad\quad (CH_3)_n \quad\quad\quad\

where n = 1 or 2 and m = 2 or 3.

3) $CH_2=C(CH_3)COOCH_2Si(CH_3)(OC_2H_5)_2 + 2CH_3COOSi(CH_3)_3 \xrightarrow{C_6H_5SO_3H} (CH_3)_3SiOSi(CH_3)(CH_2OCOC(CH_3)=CH_2)OSi(CH_3)_3 + 2CH_3COOC_2H_5$

In studying the heterofunctional cocondensation, it was found that the reaction proceeded readily to form methacrylyl siloxane compounds, with the evolution of ethyl acetate, at a temperature of ~20° if ethylsulfuric acid, containing not less than 2 weight % of water (calculated on the total amount of reacting silicoorganic compounds), was used as catalyst. The properties of the compounds obtained are given in Table 2. A detailed

TABLE 2

Formula	B.p. (at 2 mm Hg) °C	d_4^{20}	n_D^{20}	MR found	MR calc.	Bromine number found	Bromine number calc.	Si % found	Si % calc.
$(CH_3)_3SiOSi(CH_3)(CH_2OCOC(CH_3)=CH_2)OSi(CH_3)_3$	90–91	0.9170	1.4150	87.39	87.46	49.1	50.0	26.00	26.23
$CH_2=C(CH_3)COOCH_2Si[OSi(CH_3)_2CH_2OCO(CH_3)(CH_2CH=CH_2)]_2$	147–148	0.9862	1.4390	107.36	107.20	78.6	79.2	20.59	20.82
$CH_2=C(CH_3)COOCH_2Si[OSi(CH_3)_2CH_2OCO(CH_3)(CH_2CH=CH_2)]_3$	162–163	0.9953	1.4360	125.45	125.84	65.5	67.0	23.52	23.43
$CH_2=C(CH_3)COOCH_2Si[OSi(CH_3)_2CH_2OCO(CH_3)(CH_2CH=CH_2)]_4$	177–178	0.9941	1.4330	144.30	144.48	57.3	57.9	25.10	25.36

description of the synthesis of the unsaturated silicoorganic compounds obtained is given in another article.* The methacrylyl compounds synthesized are being studied in order to prepare silicoorganic polymers and block polymers.

EXPERIMENTAL

Preparation of methacryloxymethylalkoxysilanes.

A reaction mixture consisting of 0.26 mole of chloromethylalkoxysilanes (38.1 g of chloromethyldimethylethoxysilane, 45.5 g of chloromethylmethyldiethoxysilane, 45.0 g of chloromethyldimethylbutoxysilane, 59.6 g of chloromethylmethyldibutoxysilane or 74.1 g of chloromethyltributoxysilane), 37.2 g (0.3 mole) of potassium methacrylate, 5 g of copper (as a powder) and 0.3 g of hydroquinone was placed in a 150 ml autoclave. The autoclave was rotated and heated at 180° for 3.5 hours. The autoclave was cooled and opened and the reaction mixture quickly filtered to remove KCl and unreacted $CH_2=C(CH_3)COOK$ and vacuum distilled. A fraction was collected, boiling over a range of 3° (1° higher and lower than the corresponding temperature given in Table 1). The methacryloxymethylbutoxysilanes could also be prepared by heating the reaction mixtures for 2 hours at their boiling points under normal conditions. The yield was 30%.

Preparation of 1,3-dimethacryloxymethylhexamethyltrisiloxane, 1,4-dimethacryloxymethyloctamethyltetrasiloxane, 1,5-dimethacryloxymethyldecamethylpentasiloxane and 2-methacryloxymethylheptamethyltrisiloxane. A reaction mixture consisting of 12.1 g (0.06 mole) of methacryloxymethyldimethylethoxysilane and 4.4 g of dimethyldiacetoxysilane, 6.25 g of 1,2-diacetoxytetramethyldisiloxane (d_4^{20} 1.0232, n_D^{20} 1.4010) or 8.1 g of 1,3-diacetoxyhexamethyltrisiloxane (d_4^{20} 1.0131, n_D^{20} 1.4030), respectively, or a reaction mixture

* Submitted to the "Bull. Acad. Sci. USSR, Div. Chem. Sci."

consisting of 11.6 g (0.06 mole) of methacryloxymethylmethyldiethoxysilane and 28.8 g (0.12 mole) of trimethylacetoxysilane was placed in a 75 ml, round-bottomed flask, fitted with a mechanical stirrer, a thermometer, a dropping funnel and a condenser. The flask was cooled with water and the mixture stirred while 5 or 10 weight % (for the preparation of 2-methacryloxymethylheptamethyltrisiloxane) of ethylsulfuric acid, containing 2 weight % of water, was added dropwise over a period of 10-15 minutes. When the ethylsulfuric acid had been added, the reaction mixture separated into two layers, the stirring was stopped and the mixture was left for 48 hours at a temperature of ~20°. At the end of this period, the lower layer (ethylsulfuric acid) was separated with a separating funnel. The ester layer was neutralized with $NaHCO_3$ and then distilled. Ethyl acetate distilled off first and the residual layer was then vacuum distilled. In the distillation, fractions were collected, boiling at the temperatures given in Table 2. The yield was 25-33%.

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A SINGLE MECHANISM FOR THE SYNTHESIS OF HYDROCARBONS AND OXYGEN-CONTAINING COMPOUNDS FROM CO AND H_2

Iu. B. Kriukov, A. N. Bashkirov, V. K. Butiugin, L. G. Liberov and N. D. Stepanova

(Presented by Academician A. V. Topchiev December 26, 1957)

Investigators working in the field of synthesis from CO and H_2 have put forward various schemes for the synthesis mechanism according to which hydrocarbons, on the one hand, and oxygen-containing compounds, on the other, are formed by two independent reaction processes [1-5]. However, experimental data [1, 6-9] has been obtained which seem to indicate the existence of a definite single mechanism in the initiation process of the synthesis and in the build up of carbon chains of aliphatic compounds from CO on treatment with hydrogen.

To obtain such direct experimental proof of a single mechanism for hydrocarbon and alcohol formation from CO and H_2 would be extremely valuable. With this aim, the present work was devoted to studying the modes of conversion of alcohols under actual synthesis conditions, the main synthesis products being a mixture of hydrocarbons and alcohols. As indicators to follow the behavior of alcohols formed from CO and H_2, we used butanol and methanol, labeled with C^{14}, which were added to the synthesis gas in such amounts as not to disturb the conditions on the catalyst surface.

The experiments were carried out with molten iron catalysts at high pressures (100-150 atm.) under conditions that ensured the formation of approximately equal amounts of hydrocarbons and oxygen-containing compounds (mainly alcohols). The reaction products formed were separated into hydrocarbons and alcohols and then distilled on a fractionating column. The fractions from C_1 to C_9 and the residue were analyzed radiometrically by the method used previously [10].

Fig. 1 shows typical results obtained on adding butanol-1-C^{14} to the initial gas mixture.

Under the given conditions the butyl alcohol had low reactivity. The bulk of the labeled butanol introduced (90-95%) passed through the reaction zone without change. In spite of that, it has been clearly shown that labeled (and, consequently, unlabeled) butyl alcohol may participate to a certain extent in the formation of higher alcohols and corresponding hydrocarbons. However, the specific activity of butanol on discharge from the reactor was, in that case, about 400 counts/min per mg $BaCO_3$ while the specific activity of the subsequent fractions was in terms of single counts. These data indicate that less than a hundredth of the hydrocarbons above C_4 and alcohols $C_6 - C_9$ could have formed with the participation of butanol.

Thus, the overall radioactivity balance and a comparison of the specific activities indicate unequivocally that butanol is not an intermediate in the synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and hydrogen on molten iron catalysts. Under these circumstances, the presence of radioactivity in the hydrocarbons and alcohols (which have, in addition, the same order of specific activity) may be explained by the intermediate participation of some oxygen-containing complex, formed, though to a small degree, from butyl alcohol by reaction with the catalyst surface. This complex, apparently, is similar to the complex formed during the synthesis on the catalyst surface from CO and H_2 which caused the growth of the carbon chain. Both hydrocarbons and alcohols formed from this complex and as the carbon chain grew the activity, naturally, should decrease and this was actually observed.

On this basis, the anomalously high value of the specific activity of amyl and hexyl alcohols indicates

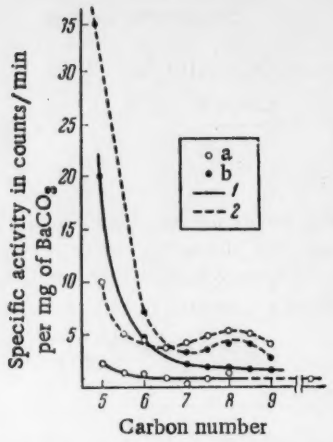


Fig. 1. Specific activity of hydrocarbons (a) and alcohols (b) in relation to the carbon number (experiments with butanol with a specific activity of 780 counts/min per mg of $BaCO_3$), 1 – Butanol concentration of 0.04 vol. %; synthesis conditions 150 atm, 200°; volume rate $1CO + 2H_2$ equal to 2000 hr^{-1}; specific activity on discharge from the reactor: butanol 386 counts/min, CO_2 3.8 counts/min, CO 0 counts/min; 2 – butanol concentration of 0.1 vol. %; synthesis conditions 90 atm., 160-180°; volume rate $1CO + 4H_2$ equal to 500 hr^{-1}; specific activity on discharge from reactor: butanol 460 counts/min; CO_2 4.9 counts/min; CO 0 counts/min; butylene 0.15 counts/min.

the existence of an independent course of alcohol conversions, which does not depend on the main course of the synthesis. These conversions, apparently, are similar to the homologization of alcohols. The radioactivity caused by this series of conversions naturally fell sharply on going from the lowest to the highest alcohol and could hardly be detected from heptyl alcohol onwards.

The activity observed in alcohols $C_7 - C_9$, like the activity in the hydrocarbons, was due to the growth of the oxygen-containing complex from which both hydrocarbons and alcohols were formed.

In experiment 2, when the concentration of radioactive butanol in the reaction mixture was increased 2.5 times (in comparison with experiment 1) naturally the specific activities of all the fractions obtained rose and the alcohol side-reactions appeared to a greater extent (see Fig. 1). A maximum of specific activity appeared in a chain with 8 carbon atoms, which indicated that under favorable conditions, intermolecular condensation of alcohols, in particular, of butanol, or of the 2 surface complexes of C_4 was possible.

Under the given conditions butanol was dehydrated only to a very small degree and therefore the observed radioactivity distribution cannot be explained by butylene reactions and this was confirmed by the results of studying the behavior of butylene under analogous conditions [11].

From the point of view of a single mechanism, it was particularly interesting to study the behavior of methanol under conditions of synthesis from CO and H_2, as the latter may react with the catalyst to form a substance containing only one C atom.

The data obtained (Fig. 2) show that under the synthesis conditions, methanol reacts in various ways much more readily than butanol: methanol decomposes to a great extent to form carbon monoxide and hydrogen, it is oxidized to carbon dioxide and participates in the synthesis of alcohols and hydrocarbons. More than 1/10th of all the hydrocarbons and alcohols could have been formed with the participation of methanol. The specific radioactivity of the hydrocarbons and alcohols with the same chain length was practically the same, proving their common origin.

However, there was not only a quantitative but also a qualitative difference in the behavior of methanol and butanol: the character of the participation of alcohols in the formation of carbon chains differed essentially. The specific radioactivity in the synthesis products remained the same regardless of the length of the chain. The molar radioactivity increased linearly with the growth of the length of the molecule. This indicated that methanol participated not only in the initiation of the carbon chain growth but also in the growth itself, being repeatedly and regularly included in the growing chain. However, a comparison of the specific activity of methanol (300 counts/min per mg of $BaCO_3$) with that of the other synthesis products (average 44 counts/min) showed that the intermediate product was not methanol itself, but some surface compound which formed quite readily from methanol. This surface complex was, apparently, similiar or even identical to the first complex formed on the catalyst surface during synthesis from CO and H_2, which was responsible for the growth of the carbon chain.

The combined data obtained show that the processes of hydrocarbon and oxygen-containing-compound synthesis from CO and H_2 are interrelated. The hydrocarbons and alcohols have the same origin when synthesized from CO and H_2 on molten iron catalysts. They originate from an unstable, intermediate complex on

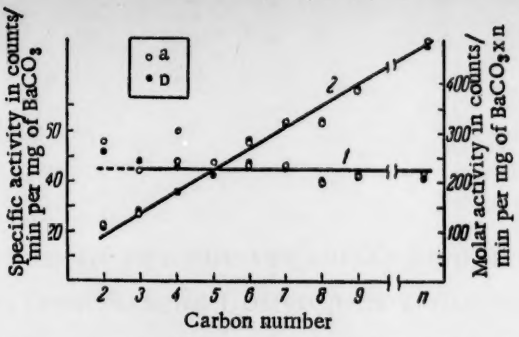
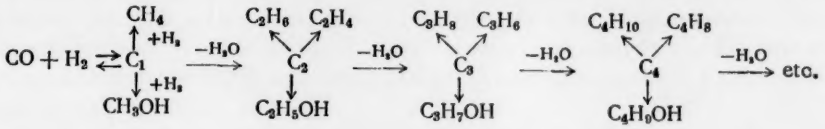


Fig. 2. Specific (1) and molar (2) radioactivities of hydrocarbons (a) and alcohols (b) in relation to the carbon number (experiment with methanol with specific activity of 3000 counts/min per mg of $BaCO_3$; experimental conditions: 90 atm., 210-220°; volume rate $CO + H_2$ equals 1600 hr^{-1}; specific activity on discharge from the reactor: methanol 300 counts/min, CO_2 75 counts/min, CO 12 counts/min.

the catalyst surface, which is formed by the primary interaction of CO and H_2 and contains C, H and O atoms. This intermediate complex (C_1) may condense with a similiar complex and thus form carbon-carbon bonds and a new oxygen-containing intermediate compound with two carbon atoms C_2. Further growth is due to subsequent addition of the first intermediate product C_1 to the growing complexes C_2, C_3, C_4 etc.



It should be pointed out that besides the mechanism put forward for the growth of the carbon chain, based directly on the experimental data obtained, these is also the possibility that CO and H_2 molecules, that have not yet been bonded in the first complex may react with the growing complex and be included in the growing chain. Probably, the larger aggregates C_2, C_3, C_4 etc. may also combine, although under the conditions studied this method of growth has a minor role. The given chain grows continuously on the catalyst surface until, due to more or less complete hydrogenation of the growing complex or to its rearrangement and desorption, a stable compound is formed – aldehyde, alcohol, olefin or paraffin. The alcohol or hydrocarbon (olefin or paraffin) once formed cannot act as an intermediate. But on coming into contact again with the catalyst surface it can undergo the secondary conversions noted above and the extent of these would depend on the catalyst properties and synthesis conditions. Alcohols may also be partially converted into the intermediate complex from which they were formed during synthesis from CO and H_2. The alcohols will be included in the chain growing on the catalyst surface in proportion to the extent to which they can generate this intermediate complex.

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THE POTASSIUM CONTENT OF SALT DEPOSITS IN TUVA

I. N. Lepeshkov, N. N. Romasheva and V. K. Solov'ev

(Presented by Academician I. I. Cherniaev September 14, 1957)

There are salt lakes and springs in the territory of the Tuva Autonomous Region and the Tuz-Tag (Salt Mountain) salt deposit, situated in the foothills of the southern slope of the Western Tannu-Ol range, 160 km south-west of the town of Kyzyl (Fig. 1), has been known for a long time.

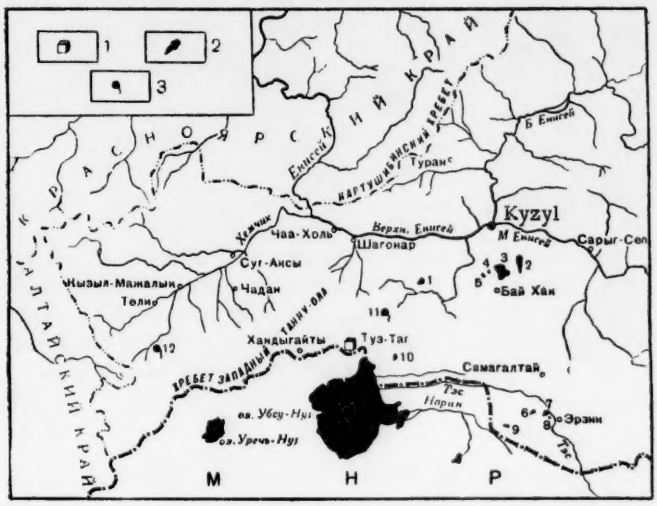

Fig. 1. Schematic map of the Tuva Autonomous region. a – Salt deposit, b – salt and weakly mineralized lakes: 1 – Khak, 2 – Chadyp, 3 – Khadyn, 4 – Svatkova, 5 – Kach-Khol', 6 – Dus-Khol' I, 7 – Dus-Khol' II, 8 – Kak-Khol' II, 9 – Shara Nur, 10 – Amangeidyn-Khol'; c – sources of salt springs on the northern slope of the Tannu-Ol Range: 11 – on the Khurgecha R., 12 – on the Tustukhem R.

There is data in the literature on some of the Tuva lakes and on the Tuz-Tag salt deposit [1-4]. We first investigated the salt lakes and salt deposits of Tuva in 1953. We described the physico-chemical characteristic of the salt and weakly mineralized Tuva lakes in paper [5]. In this article we give the characteristics of the Tuz-Tag salt deposits, paying special attention to the potassium and other salts of a marine type.

The Tuz-Tag salt deposits are the results of the existence of sea basins on the Tuva territory in the Upper Silurian and Lower Devonian geological periods (Fig. 2). The total width of the Tuz-Tag salt deposits is over 300 m [6]. The Tuz-Tag salt seams lying at an angle of 40-45°, appear at the surface. Rock salt has been mined from the deposit for a long time and there is a series of pits (exhausted mines) up to 3-5 m deep. We examined

the salt seams that appeared at the surface and took samples for investigation. The salt was grey in four of the salt seams and in only one middle seam, besides the grey salt, were there layers of pink, lemon-yellow and meat-red color (the width of the layers was 3-10 cm). Such salt colors are characteristic of natural potassium salts.

Chemical investigation of the salt samples, taken from these layers, showed a considerable amount of potassium chloride (up to 65%).

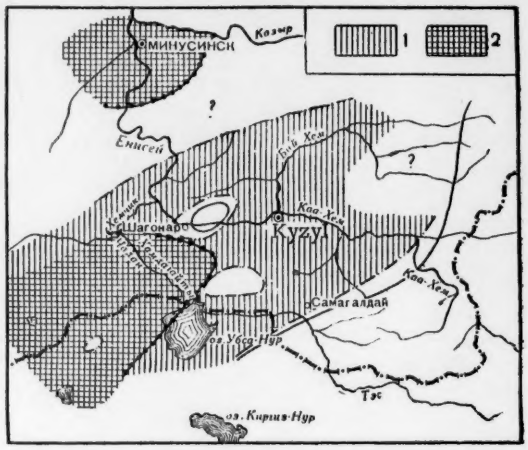

Fig. 2. Map showing the distribution of sea basins in the Tuva territory and neighboring regions. 1 – Upper Silurian sea basin; 2 – Lower Devonian sea.

Table 1 gives the chemical analysis of some of the potassium salts, taken from a central pit. As the analyses show, the salt samples are sylvinites containing a large amount of potassium chloride. In connection with the discovery of a high potassium chloride content in some of the salt samples from the salt seams of the Tuz-Tag deposit, we examined the salt cores, lifted in 1951 by a mining-geological expedition, from bores in the Tuz-Tag deposit. We selected 100 salt samples from 8 bores from various depths.

TABLE 1

No. of sample	KCl	$MgCl_2$	NaCl	$CaSO_4$	$CaCl_2$	Water-insoluble residue	Total salt	Salt color
	in weight percent							
74	65.63	2.58	21.90	3.39	—	4.09	97.59	Lemon-yellow
71	43.91	0.86	52.43	0.64	0.11	1.39	99.34	Meat-red
70	10.09	—	72.72	0.48	0.61	15.08	98.98	Pink

A general examination of the preserved cores showed that besides the grey rock salt, some cores had yellow, pink and red salts in them. Many of the cores, especially those that were pink, dark red and yellow were strongly eroded, probably due to the washing through of the bores during drilling. The potassium and magnesium salts could have been washed out, to a considerable degree, from the salt cores.

The data from chemical analyses showed that the salt cores from bores Nos. 7 and 8 and from a depth of 15 to 105 m contained the most potassium. The potassium chloride content in separate samples, taken from a core, was 16-39%.

The chemical analyses of potassium inclusions in salt cores from bores Nos. 5, 7 and 8 are given in Table 2.

The potassium salts in these samples are in the form of sylvinite, as in the samples we collected from the salt seams that emerged at the surface.

It should be noted that the mining-geological expedition did not find considerable amounts of potassium salts in the cores probably due to the fact that the average sample was analyzed without detailed investigation of separate samples and of sections containing potassium.

TABLE 2

No. of sample	No. of bore	Depth in m	KCl	NaCl	$CaSO_4$	$CaCl_2$	$MgCl_2$	Water-insoluble residue	Total salts
			in weight percent						
187	8	16. 5—18.3	39.56	56.58	0.90	0.18	—	1.47	98.79
189	8	23.30—24.30	1.98	95.72	0.50	0.03	—	0.45	98.68
180	7	59.1—68.8	16.21	77.27	1.06	0.32	—	4.26	99.12
183	7	90.7—100.1	3.77	69.42	0.46	1.69	1.26	17.55	94.15
185	7	100.1—106.5	2.55	44.00	5.85	0.10	—	46.21	98.71
171	5	38.2—40.2	1.83	96.23	0.38	0.08	—	0.73	99.25

We consider that the data obtained merit attention and should raise the question of a further, more detailed study of the Tuz-Tag salt deposits in order to find the beds of potassium, magnesium and other sea salts.

N. S. Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences USSR

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PREPARATION OF SOME PRIMARY ALCOHOLS VIA ORGANOALUMINUM COMPOUNDS

A. M. Sladkov, V. A. Markevich, I. A. Iavich,
L. K. Luneva and V. N. Chernov

(Presented by Academician B. A. Kazanskii December 27, 1957)

As the possibility of preparing alcohols via organoaluminum compounds was reported in the literature [1], we investigated a series of reactions in which α-olefins were converted into primary alcohols by the schemes:

1) $R-CH=CH_2 + al + H \rightarrow R-CH_2-CH_2-al$ (I)
2) (I) $+ O_2 \rightarrow R-CH_2CH_2-O-al$ (II)
3) (II) $+ H_2O \rightarrow RCH_2CH_2OH +$ al (OH), where al $= 1/3$ Al

We carried out reaction 1 with 2-methylpentene-1 and 2-ethylhexene-1, which were prepared by dimerization of propylene and n-butylene. The trialkylaluminums from these olefins and triethylaluminum, synthesized by another method, were oxidized with air into alcoholates, which were hydrolyzed to the corresponding alcohols. A special experiment on the oxidation of tridecylaluminum at a low temperature showed that the reaction proceeded through the formation of a peroxide compound which, apparently, underwent an intermolecular rearrangement or reacted with alkylaluminum to give the aluminum alcoholate:

$$R_3Al + O_2 \rightarrow R-OO-AlR_2$$
$$R-OO-AlR_2 \rightarrow (RO)_2AlR \text{ etc.}$$
or $$R-OO-AlR_2 + R_3Al \rightarrow 2ROAlR_2 \text{ etc.}$$

The investigation results showed that alcohols may be obtained through alkylaluminums relatively simply and in quite high yields (60-65%).

The hydrogenation products of the olefins were always formed as side products during the formation of the trialkylaluminums. Thus 2-methylpentene-1 gave 2-methylpentane and 2-ethylhexene-1 gave 2-ethylhexane. The hydrogenation was apparently due to the presence of finely dispersed iron in the active aluminum, which acted as a specific catalyst of a similar type to the skeletal forms of metals from the 8th group of the periodic table. The iron content of some aluminum samples was 12-15%.

A much higher reaction temperature was required to dimerize butene-1 (by 100°) than was required for propylene.

Preliminary results of analysis of the resulting gas from the dimerization showed that butene-2 hardly entered the reaction. In addition to 2-ethylhexene-1, hexene-1 (from butylene and triethylaluminum) and 2-methylpentene-1 (from propylene in the technical butylene fraction) were always formed. Despite the presence of the side products, the yield of butene-1 dimer was very high (up to 90% of theoretical).

EXPERIMENTAL

Starting materials. 2-Methylpentene-1 was prepared by dimerization of propylene in the presence of

triethylaluminum by Ziegler's method [2]. The yield of a product with b.p. 62-62.5°/760 mm was 90% of the theoretical; $n_D^{20} = 1.3920$; $d_4^{20} = 0.6793$; literature data [3]: b. p. 61.5-62°/760 mm; $n_D^{20} = 1.3921$; $d_4^{20} = 0.6817$. 2-Ethylhexene-1 was prepared by dimerization of butene-1. Tridecylaluminum was synthesized by an exchange reaction between didecylmercury and metallic aluminum [4]. Triethylaluminum was prepared from ethyl iodide and magnesium – aluminum alloy by a modification of the method described in an American patent [5]. The active aluminum was used as a suspension in benzine (95-100°) with an average particle size of 1-5μ.*

Preparation of 2-ethylhexene-1. A 1 liter autoclave, fitted with a stirrer, a manometer and an electric heater, was loaded with 360 g of technical butylene fraction, containing ~40% butene-1 and 200-250 g of ligroin (b.p. 150-220°), in which was dissolved 5-10 g of triethylaluminum. The contents of the autoclave were stirred and heated to 280-295°. While this temperature was maintained the pressure began to fall and this continued for 6 hours. When the fall in pressure ceased, the autoclave was cooled and the reaction products unloaded and distilled. From the distillation we obtained 109 g of 2-ethylhexene-1 (90% of theoretical) with b. p. 118-119°/760 mm, $n_D^{18} = 1.4150$; $d_4^{18} = 0.7270$; MR calc. 38.68; MR found 38.65. Literature data [6]: b. p. 120°/760 mm, $d_4^{20} = 0.7270$; $n_D^{20} = 1.4157$.

Synthesis of triethylaluminum. Into a four-necked flask, fitted with a stirrer, a reflux condenser, a dropping funnel and a gas inlet tube, was placed 65 g of powdered alloy, consisting of stoichiometric amounts of aluminum and magnesium. The reaction was performed in a slow stream of dry nitrogen, freed from oxygen. The contents of the flask were heated on an oil bath to 70-80° and 2-5 ml of ethyl iodide was introduced at this temperature to initiate the reaction. The reaction usually started at once. When all the ethyl iodide had reacted, as indicated by the disappearance of drops dripping from the condenser into the flask, a further 300 g of ethyl iodide was gradually added in portions of 10-15 ml. Each successive portion of ethyl iodide was added after the previous portion had reacted.

When all the ethyl iodide had been added, the reaction mixture was heated for a further hour. The flask was cooled in a stream of nitrogen, a mineral oil (for example, type VM-4) added and the triethylaluminum distilled off from the reaction flask under reduced pressure, after replacing the stirrer with the mercury seal by a Wurtz still head. The yield of triethylaluminum was 80% of theoretical, calculated on the ethyl iodide.

Preparation of higher trialkylaluminums. 2 moles of 2-methyl pentene-1 or 2-ethylhexene-1 and a two-fold excess of a suspension of aluminum in benzine, activated with 2-5% of triethylaluminum, was placed in an autoclave. The reaction mixture was heated to 120-130° and at this temperature, dry, oxygen-free hydrogen was introduced into the autoclave to a pressure of 50-70 atm. As the pressure fell, successive portions of hydrogen were introduced until the pressure no longer fell. The reaction mixture was stirred for a further hour and then the autoclave was cooled and the product unloaded into an inert atmosphere.

Oxidation of trialkylaluminums and hydrolysis of alcoholates. The reaction mixture from the previous experiment was decanted from the precipitate and placed in a conical flask, fitted with a stirrer, a reflux condenser, a thermometer and an air inlet, extending almost to the bottom of the flask.

With rapid stirring, a stream of air was passed at such a rate that the temperature did not exceed 65-70°. The air was passed continuously until the temperature fell to 30°, when oxygen was passed for an hour; with this the temperature at first rose to 50-60° and then fell. After the temperature had ceased to fall, the introduction of oxygen was stopped and the air inlet tube replaced by a dropping funnel, through which dilute (10-20%) hydrochloric acid was added, at first dropwise and then in larger portions. After the hydrolysis the upper oily layer was separated, dried over anhydrous potassium carbonate and distilled.

From 2-methylpentene-1 we obtained 2-methylpentanol (yield 60% of theoretical, calculated on the 2-methylpentene-1, and 54% of theoretical, calculated on propylene) with b. p. 145-147°/744 mm, $n_D^{21} = 1.4171$; $d_4^{21} = 0.8224$; literature data [7, 8]: b. p. 148°/762 mm; $n_D^{20} = 1.4182$; $d_4^{20} = 0.8263$; MR found 31.24, MR calc. 31.43.

* We would like to take this opportunity to thank A. F. Zhigach for providing us with samples of active aluminum.

Correspondingly, from 2-ethylhexene-1 we obtained 2-ethylhexanol-1(yield 58%, calculated on butene-1, and 65% of theoretical, calculated on ethylhexene) with b.p. 183-184°/760 mm, n_D^{18} = 1.4310, d_4^{18} = 0.8344; literature data [9]: b. p. 184.2-185°/760 mm; n_D^{20} = 1.4313; d_4^{20} = 0.8324.

Oxidation of triethylaluminum and hydrolysis of aluminum ethylate. The reaction was performed with the reaction mixture cooled to -15°. Air was first passed at such a rate that the temperature did not rise above -5°, then the air flow was increased somewhat and the oxidation continued for an hour at room temperature. The oxidation was completed by heating the reaction mixture to 40-50° (2 hours).

The reaction products were hydrolyzed as described above. Distillation on a column yielded 20.3 g of ethyl alcohol as the azeotrope with water (b.p. 78° at 756 mm). The yield of ethyl alcohol was 80% of theoretical.

Oxidation of tridecylaluminum. A 10% solution of tridecylaluminum in isopentane was oxidized by passing oxygen at -70° for 5 hours. The reaction mixture was poured into a 10% aqueous solution of sodium hydroxide at -10° with vigorous stirring. The aqueous (alkaline) layer was saturated with carbon dioxide and then the aqueous layer was extracted with ether. The ether solution gave a definite reaction for hydroperoxides (iodometric determination).

Institute for Research on Synthetic Alcohols
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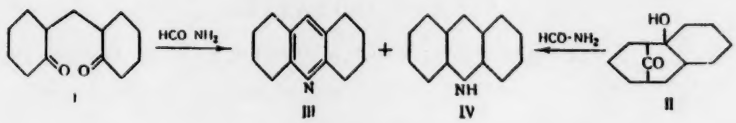
THE EFFECT OF FORMAMIDE ON ISOMERIC METHYLENEDICYCLOHEXANONE AND TRICYCLOHEXANOLONE

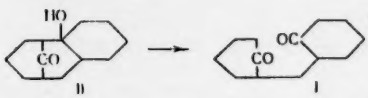
M. N. Talichenko and V. I. Vysotskii

(Presented by Academician B. A. Kazanskii December 23, 1957)

Formamide reacted with methylenedicyclohexanone (I) [1, 2] and with its isomer, tricyclohexanolone (II) [1], which were described recently, under the conditions of the Leikart reaction to give the same compounds in both cases, namely: sym-octahydroacridine (III) and perhydroacridine (IV):



This indicated that under the reaction conditions, II was isomerized to I:



and that the process proceeded at quite a rapid rate (otherwise the main reaction products would have been the products of hydroamination of II).

The reaction found is also of value from the preparative point of view: it proceeds quite smoothly, giving a good yield of the base (~80%), is technically simple to perform and the starting materials are readily available. This indicates its advantages over earlier methods of preparing these bases [3-5].

Finally, it should be noted that it is the first example of applying the Leikart reaction to alicyclic 1,5-diketones. Previously, the Leikart reaction was carried out with several 1,5-diketones of the aliphatic and arylaliphatic series [6, 7].

EXPERIMENTAL

The experiments with the diketone (I) and the ketol (II) were performed under completely identical conditions. A solution of one of the compounds (1 mole) in formamide • (12 moles) was heated in a flask with a reflux air condenser at 155-170° (thermometer in mixture) until the evolution of CO_2 ceased (~4 hrs). The hot solution was then poured into 5-6 times its volume of ~10% aqueous sodium hydroxide and boiled on gauze for about 2 hours. After cooling, the oil which separated was extracted with benzene or ether. The extract was dried with baked magnesium sulfate. The residue from evaporating off the solvent was vacuum distilled:

52% came over at 98-105°/2.5 mm (1st fraction)
14% came over at 113-116°/0.5 mm (2nd fraction)
33.5% remained in the distillation flask; this residue quickly crystallized.

• The formamide was prepared according to [8].

sym-Octahydroacridine ($C_{13}H_{17}N$). The crystalline residue was pressed on a porous plate and recrystallized from petroleum ether, when it had a constant melting point of 69.5°. Literature data: 69° [3, 4]; 73.5-74° [5]; 71° [9]; 68-70° [1]. A mixture of it with a standard sample of sym-octahydroacridine, prepared by the method in [1], did not have a depressed melting point.

Found %: N 7.75; M 189. $C_{13}H_{17}N$. Calculated %: N 7.50; M 187.

The picrate had m.p. 197.5-199° (from alcohol) and did not depress the melting point of the picrate of a standard sample.

Perhydroacridine ($C_{13}H_{23}N$). The distillate (both fractions) crystallized on distilling over. After being pressed on a porous plate and recrystallized from petroleum ether, the crystals formed white needles with a constant melting point of 87-88.5°. Literature data for perhydroacridine: 80° [3], 91° [5].

Found %: C 80.60; 80.57 H 11.90; 12.10; N 7.18; 7.26; M 192; 189. $C_{13}H_{23}N$. Calculated %: C 80.82; H 11.91; N 7.25; M 193.

The picrate formed yellow, needle-like crystals with m.p. 179-181° (from alcohol).

Acetylperhydroacridine was formed on evaporating down a mixture of 0.7 g of the base and 1 ml of acetic anhydride in vacuum on a boiling water bath. The residue (0.45 g) crystallized. The colorless, quadrangular or hexagonal plates (from alcohol) decomposed without melting in the range 150-160° when heated in a capillary.

Found %: CH_3CO 17.73. $C_{13}H_{22}NCOCH_3$. Calculated %: CH_3CO 18.30.

Perhydroacridine hydrochloride formed readily on treating the base with concentrated hydrochloric acid. The white, needle-like crystals (from alcohol) were difficultly soluble in water and cold alcohol and insoluble in benzene. On being heated in a capillary, they decomposed at 220-230° without melting.

Found %: Cl 15.30. $C_{13}H_{23}NHCl$. Calculated %: Cl 15.47.

Reduction of octahydroacridine to perhydroacridine. The octahydroacridine obtained was reduced very smoothly by sodium in absolute alcohol in the presence of catalytic amounts (~ 3% of the base taken) of nickel formate to give perhydroacridine. The perhydroacridine obtained in this way was identical (mixed melting point) with that described above.

We were unable to obtain good yields of perhydroacridine in the absence of nickel formate.

N. G. Chernyshevskii State University of Saratov

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SYNTHESIS OF ALKYLINDANS

Academician A. V. Topchiev, E. S. Pokrovskaia and T. G. Stepantseva

The preparation of pure hydrocarbons, whose boiling points correspond to the kerosene and oil fractions of petroleum, and a thorough study of their properties is a necessary preliminary stage in the complicated problem of investigating the hydrocarbon composition of these petroleum fractions. Of the aromatic hydrocarbons, which could be present in the middle petroleum fractions, the hydrocarbons of the indan series have not been studied sufficiently.

Individual alkylindans are described in the literature and these were mainly prepared by closing the five-membered ring, but the systematic synthesis and study of these hydrocarbons is still only in the first stage. The only paper which can be regarded as a systematic investigation is that by Entel et al. [1], who prepared some methyl- and dimethylindans by closing the five-membered ring and determined the absorption spectra in the infrared and ultraviolet regions in addition to the usual properties of these hydrocarbons.

In order to complete the information on the properties of indan hydrocarbons and obtain preparations for spectral investigations, we undertook the synthesis of the hydrocarbons of this series and first of all, the alkylindans with aliphatic substituents in the aromatic ring.

Up to now alkylation of the hydrocarbon in the synthesis of indan homologs has been used in only a few cases and is described in a few papers. Kurtz et al. [2] alkylated indan with ethylene, propylene and isopropylenyl alcohol in the presence of $Al_2O_3 \cdot SiO_2$ under pressure and at a high temperature (250-300°) and obtained in this way ethylindan, isopropylindan and indan condensation products. Butylindan was synthesized by alkylating indan with tertiary butyl chloride in the presence of aluminum chloride. However, the purpose of this work was to prepare nitro derivatives of this hydrocarbon and not to study its properties, so the authors only gave the boiling and solidification points of tertiary butylindan [3].

Indan reacted with cyclohexene very smoothly to give a good yield in the presence of aluminum chloride at atmospheric pressure and a temperature of about 5°. Mono-, di- and tricyclohexylindans were synthesized under these conditions [4]. Mono and dicyclopentylindans were prepared in the same way, starting with indan and cyclopentene [5].

To prepare the starting material, indan, we hydrogenated indene over Raney nickel catalyst at normal termperature and a starting hydrogen pressure of 150-120 atm. [6]. After distillation over metallic sodium, the indan had b.p. 177°, $n_D^{20} = 1.5390$, $d_4^{20} = 0.9640$, which agrees with the literature data: b.p. 176.7°, $n_D^{25} = 1.5355$, $d_4^{25} = 0.9604$ [1].

As the alkylation of indan with cycloolefins in the presence of aluminum chloride proceeded smoothly and gave only the products of substitution in the aromatic nucleus [4, 5] we used this method for preparing indan homologs with side chains of the aliphatic series.

Indan was alkylated with the olefins propylene, butylene-1 and trimethylethylene in a glass reactor with continuous stirring and cooling with ice. The gas was passed through at a rate of 2-4 liters/hour; trimethylethylene was added dropwise; the aluminum chloride, 1/2-1/4 of the olefin weight, was added in portions. The thin layer of hydrocarbon – aluminum chloride complex formed was separated from the main layer of the reaction products, which were then treated in the usual way and distilled several times on a column of 12 theoretical plates. The reaction product yields given are calculated on the olefin used.

Using the methods described, indan and propylene, taken in molecular ratios of 1 : 0.5and 1 : 1.5 (with 300 g total amount of indan), gave ~50% yield of reaction products, calculated on propylene, and several fractionations of these gave the following fractions: one with b.p. 62°/2 mm, corresponding to isopropylindan $C_{12}H_{16}$ (analysis) and another with b.p. 83-85°/2 mm, corresponding to diisopropylindan $C_{15}H_{22}$ (analysis). The properties of these hydrocarbons and all those described below are given in Table 1. Alkylation of a wide monoisopropylidene fraction with b.p. 228-233°, using propylene, gave a solid triisopropylindan $C_{18}H_{28}$ (analysis) and a liquid isomer with b.p. 276-280°, a solidification point below -65°, $d_4^{20} = 0.9202$ and $n_4^{20} = 1.5220$.

Under analogous conditions indan (950 g total amount) was alkylated with an equimolecular amount of butylene-1. The reaction products yielded sec-butylindan $C_{13}H_{18}$ (analysis) with b.p. 68-69°/2 mm and di-sec-butylindan $C_{17}H_{26}$ (analysis) with b.p. 121-122°/2 mm.

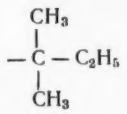
TABLE 1

Hydrocarbon	B.p., °C/mm Hg	Solid. p., °C	d_4^{20}	n_D^{20}	$\frac{n_F - n_c}{d} 10^4$	Viscosity centistokes 20°	50°	100°	Aniline p. (max.), °C
Isopropylindan $C_{12}H_{16}$	62/2 230/751	—65 No solid.	0.9347	1.5240	164.6	2.9	1.6	0.9	Below—10
Diisopropylindan $C_{15}H_{22}$	83—85/2 255—256/751	—44 Glass	0.9210	1.5183	—	7.6	3.1	1.3	Below—10
Triisopropylindan $C_{18}H_{28}$	108—109/2	45—46	—	—	—	—	—	—	—
sec-Butylindan $C_{13}H_{18}$	68—69/2 245/753	—65 No solid	0.9252	1.5213	157.5	—	—	—	Below—10
Di-sec-butylindan $C_{17}H_{28}$	122—123/2	—50 Glass	0.9068	1.5138	147.4	—	—	—	+0,5
Amylindan* $C_{14}H_{20}$	256—257/744	—56 Glass	0.9355	1.5245	151.4	6.8	2.9	1.3	Below—10
Amylindan** $C_{14}H_{20}$	257—258/744	—55 Glass	0.9350	1.5245	—	—	—	—	—
Amylindan** $C_{14}H_{20}$	81—82/2 255—257/744	—45 Glass	0.9324	1.5230	—	—	—	—	—

*Prepared with $BF_3 \cdot H_3PO_4$ as catalyst.

**Prepared with $AlCl_3$ as catalyst.

Trimethylethylene, prepared by dehydrating dimethylethylcarbinol, was used for synthesizing amylindan. The alkylation was carried out with a 3:1 ratio of the reacting substances, both in the presence of aluminum chloride, starting with 300 g of indan, and with $BF_3 \cdot H_3PO_4$ [7] catalyst, with 250 g of indan. In the first case one fraction was isolated in ~20% yield and in the second, ~40% yield of two fractions of amylindan $C_{14}H_{20}$ (analysis), whose properties differed very little (Table 1). In the first case the high boiling reaction products contained mainly indan condensation products; they did not contain diamylindan. The high boiling products of the reaction with $BF_3 \cdot H_3PO_4$ were a tarry mass and were not investigated. As the alkylation was carried out with trimethylethylene, the amyl side chain should have the following structure:



Of the hydrocarbons given in Table 1, the literature describes only isopropylinan, which is a mixture of 4- and 5-isopropylindan isomers, and its constants [2] are almost identical with those of the hydrocarbon we obtained. All the other indan homologs we describe were prepared for the first time by us. The densities andrefractive indexes of the hydrocarbons synthesized, lie within the normal range for alkylindans ($d_4^{20} = 0.92$-0.93 and $n_D^{20} = 1.51$-1.52); the aniline points of all the hydrocarbons, except dibutylindan, lie below 0°, which is usual for aromatic hydrocarbons of low molecular weight. The specific dispersion decreases linearly as the number of carbon atoms in the side chain increases.

A. P. Bogomolova participated in the work.

Institute of Fuel
Academy of Sciences USSR

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PHASE CHANGES IN THE SODIUM SULFATE – CARBONATE SYSTEM

A. N. Khlapova

(Presented by Academician I. I. Cherniaev December 31, 1957)

In contrast to [1-5], this investigation of sodium sulfate – sodium carbonate melts was carried out on the same samples simultaneously by differential thermographic, x-radiographic and crystallo-optical methods of phase analysis. The melts were studied 1-5 days after preparation, after being kept for 1-2 months without access to atmospheric moisture and after more than a year in the open air under laboratory conditions.

The results obtained are given in Figs. 1 and 2.

The phase diagram of $Na_2SO_4 - Na_2CO_3$ (Fig. 1) shows that the high temperature sodium sulfate – sodium carbonate solid solution, which crystallized from a melt of the salts, underwent a series of phase changes on cooling. The process of phase changes with temperature in this system is due, first of all, to the existence of polymorphism in sodium sulfate and sodium carbonate [6-10]. Thus a continuous series of δ-solid solutions, formed from the high temperature δ-modifications of the initial components (δ-Na_2SO_4 [6, 7] and δ-Na_2CO_3 [8]) at about 600° (the temperature of the $\delta \rightleftharpoons \gamma$ polymorphous conversions of the pure salts) in a range covering all concentrations, is converted into an inorganic γ-solid solution, which forms between γ-Na_2SO_4 [6, 7, 9] and γ-Na_2CO_3 [8, 10].

Depending on the composition of the melt, the γ-solid solution decomposes at different temperatures to form a complex curve. In the central part of the diagram at about 400° this curve has two maxima, one of which lies at 66.3 mole % Na_2SO_4 and corresponds to the formation of the binary salt with the composition $2Na_2SO_4 \cdot Na_2CO_3$ (hexagonal burkeite [11]) in the solid phase and the other at 25 mole % Na_2SO_4, corresponds to the formation of the binary salt with the composition $Na_2SO_4 \cdot 3Na_2CO_3$. Between these two chemical compounds a phase is formed with a varying composition based on hexagonal burkeite [11] (γ'-phase) and this lies at normal temperatures in the range from ~13.0 to 75.0 mole % Na_2CO_3.

As Fig. 1 shows, a limited β-solid solution is formed based on the β-modification of sodium sulfate [6] and at approximately 130° it gave a third chemical compound of sodium sulfate and sodium carbonate with the composition $9Na_2SO_4 \cdot Na_2CO_3$ (ϵ-phase). This binary salt gave practically no solid solutions with its components.

The α'- and β'-phases found in the range rich in Na_2CO_3 (Fig. 1), were limited solid solutions of sodium sulfate in the α- and β-modifications, respectively, of sodium carbonate [8, 10].

The x-radiographic and crystallo-optical characteristics of the low temperature solid phases of the $Na_2SO_4 - Na_2CO_3$ system are given in [11].

The present investigation established that the α-, β-, ϵ-, γ'-, and α'-solid phases and the binary salts with the compositions $9Na_2SO_4 \cdot Na_2CO_3$, $2Na_2SO_4 \cdot Na_2CO_3$ and $Na_2SO_4 \cdot 3Na_2CO_3$ (Fig. 1), were stable in the absence of moisture and became unstable and metastable in the presence of water vapor or under atmospheric conditions, as H_2O vapor, which reacts chemically with the two-component melts of sodium sulfate – sodium carbonate, behaves as a third component in the system in this case. Therefore, as Fig. 2 shows, all the low temperature solid phases of the $Na_2SO_4 - Na_2CO_3$ binary system (Fig. 1), tending toward an equilibrium with H_2O, are gradually converted (depending on the composition of the melt) as moisture penetrates into the crystals,

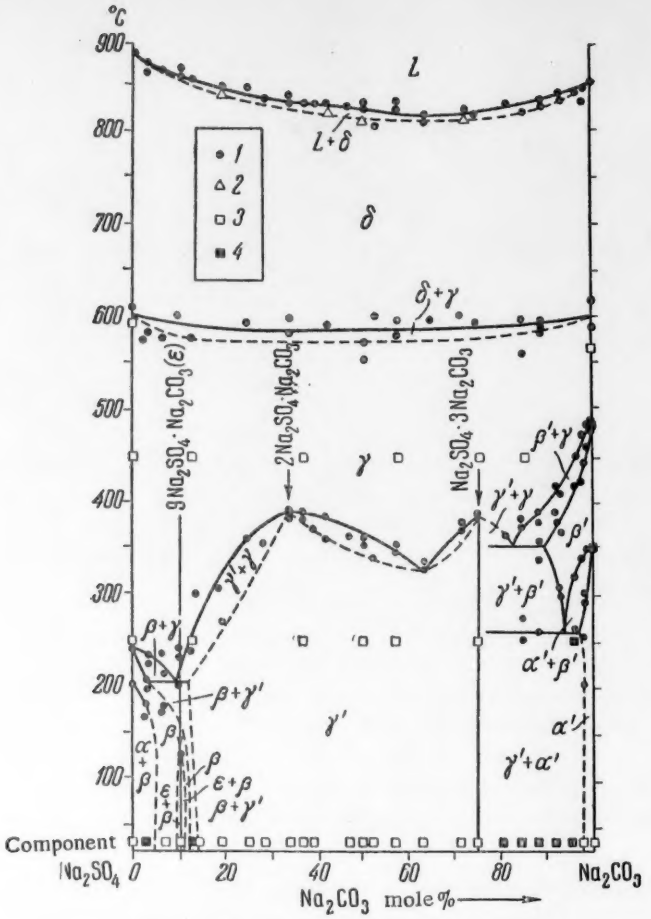

Fig. 1. Equilibrium phase diagram of melts of the Na_2SO_4–Na_2CO_3 system, protected from the effects of moisture after fusing the salts. Differential thermographic analysis data (from the heating curves of two samples): 1 – liquidus, 2 – solidus. x-Radiographic analysis data: 3 – single phase, 4 – two-phase; the γ'-phase, based on the compounds $2Na_2SO_4 \cdot Na_2CO_3$ and $Na_2SO_4 \cdot 3Na_2CO_3$, lies from 13.0 to 75.0 mole% Na_2CO_3.

into thenardite (T-phase), rhombic burkeite (γ''-phase) and sodium carbonate monohydrate (x-phase), which usually form from supersaturated aqueous solutions of the Na_2SO_4–Na_2CO_3–H_2O ternary system [2, 6, 11, 12].

Papers [6 and 11] reported that thenardite and rhombic burkeite contain a very small amount (a fraction of a weight %) of water, structurally bound in their crystals.

The present investigation has resulted in new data on the phase conversions of the Na_2SO_4 – Na_2CO_3 system and the main differences in the nature of the solid phases formed between sodium sulfate and sodium carbonate in the molten state and in aqueous solutions of these salts has been found.

It is established that in the presence of water vapor and under atmospheric conditions the sodium sulfate – sodium carbonate melts were converted from a two-component into a three-component state and the equilibrium phase diagram of the Na_2SO_4 – Na_2CO_3 binary system (Fig. 1) changed into the equilibrium phase

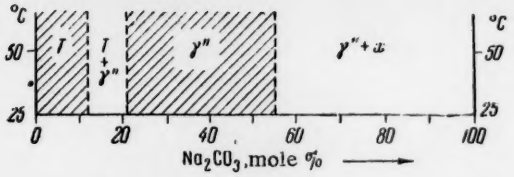

Fig. 2. Equilibrium phase diagram of melts of the Na_2SO_4 – Na_2CO_3 system in the presence of water vapor and under atmospheric conditions: T-phase with a thenardite structure, γ''-phase with a rhombic burkeite structure, x-phase with a sodium carbonate monohydrate structure.

diagram of the Na_2SO – Na_2CO_3 – H_2O ternary system (Fig. 2).

N. S. Kurnakov Institute of Organic Chemistry
Academy of Sciences USSR

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PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

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VOLUME 119, NOS. 1-6 MARCH-APRIL, 1958

CONTENTS

	PAGE	ISSUE	RUSS. PAGE
Anti-Cancer Peptides. N. E. Golubeva, O. V. Kil'disheva and I. L. Knuniants	191	1	83
x-Ray Investigation of 1,4-Dianilinoanthraquinone and 1,4-Dimesidinoanthraquinone. N. S. Dokunikhin, G. A. Gol'der and G. S. Zhdanov	195	1	87
Certain Features of Carbonium-Ion Polymerization of the System Styrene-α-Methylstyrene. E. B. Liudvig, A. R. Gantmakher and S. S. Medvedev	199	1	90
Synthesis and Properties of Mixed Esters of Phenylimidodithiocarbonic Acid. A. I. Mashentsev	203	1	94
Polymerization and Copolymerization of Unsaturated Organosilicon Compounds. p-Trialkylsilylstyrenes. V. V. Korshak, A. M. Poliakova, A. A. Sakharova, A. D. Petrov and E. A. Chernyshev	207	2	282
Equilibrium of the Condensed Phases in the System Naphthalene – Thionaphthene. V. M. Kravchenko and I. S. Pastukhova	211	2	285
Reactions of Diferrocenylmercury. A. N. Nesmeianov, E. G. Perevalova and O. A. Nesmeianova	215	2	288
The Reaction of Vinylacetylene with Diazomethane. A. T. Troshchenko and A. A. Petrov	219	2	292
The Use of Organozinc Compounds for the Synthesis of Carbon-Carbon Derivatives of Sugars. Iu. A. Zhdanov, G. N. Dorofeenko and G. V. Bogdanova	223	3	495
Investigation of the Phase Composition of Alloys of Iron with Vanadium and of Iron with Chromium. M. I. Zakharova, I. A. Ignatova, L. A. Semenova and N. A. Khatanova	227	3	498
On the Quasi-Binary System: Six-Component Nickel Solid Solution + Titanium Carbide. I. I. Kornilov, L. I. Priakhina, O. V. Ozhimkova and A. Ia. Snetkov.	231	3	501
Retention of Configuration By a Propenyl Radical During Reactions Involving Transfer From Metal to Metal. A. N. Nesmeianov, A. E. Borisov and N. V. Novikova	235	3	504
Europium Hexaboride. G. V. Samsonov, V. P. Dzeganovskii and I. A. Semashko	237	3	506
Mercuration of Polystyrene. R. N. Smirnov	239	3	508
Polymerization of Isobutylene in the Presence of Boron Trifluoride on Activated Carbon. A. V. Topchiev and L. A. Aliavdina	243	3	511
On the Composition of the Alcohols Obtained by Liquid-Phase Oxidation of n-Paraffinic Hydrocarbons. A. N. Bashkirov, V. V. Kamzolkin, K. M. Sokova and T. P. Andreeva	247	4	705
Synthesis and Transformations of Cis- and Trans-1-Ethynyl-1-Decalols. I. N. Nazarov, G. V. Aleksandrova and A. A. Arkhem	251	4	708

(continued)

CONTENTS (continued)

	PAGE	ISSUE	RUSS. PAGE
Retention of Configuration of the Propenyl Radical in Reactions of Cis- and Trans-Propenyllithium with Oxo Compounds. A. N. Nesmeianov, A. V. Borisov and N. V. Novikova	257	4	712
Dehydrocyclization of n-Heptane Over Chrome-Alumina Catalysts. M. I. Rozengart and B. A. Kazanskii	261	4	716
Polymerization of Isobutylene by the Action of Boron Trifluoride Adsorbed on Silica Gel. A. V. Topchiev and L. A. Aliavdina	265	4	720
Determination of the Purity and Crystallization Temperature of Some Hydrocarbons Using 1-2 ml Samples. A. G. Anikin and G. M. Dugacheva	269	5	939
Types of Structural Diagrams of Ternary Systems Based on Titanium. I. I. Kornilov and P. B. Budberg	273	5	942
Stereochemistry of the Diene Condensation of 1-α-Acetoxyvinyl-Δ^1-Cyclohexene with Maleic Anhydride. I. N. Nazarov, V. F. Kucherov, V. M. Andreev and G. M. Segal'	277	5	945
Reactions of Ferrocenesulfonic Acids. A. N. Nesmeianov, E. G. Perevalova, S. S. Churanov and O. A. Nesmeianova	281	5	949
The Nature of the Water in Heteropoly Compounds of Tungsten Heteropoly Acids. E. Ia. Rode	285	5	953
Polymerization of Isobutylene Under the Influence of Boron Trifluoride on Aluminum Oxide. A. V. Topchiev and L. A. Aliavdina	291	5	957
Synthesis of Silicoorganic Compounds Containing Methacrylyl Groups. K. A. Andrianov and A. K. Dabagova	295	6	1149
A Single Mechanism for the Synthesis of Hydrocarbons and Oxygen-Containing Compounds From CO and H_2. Iu. B. Kriukov, A. N. Bashkirov, V. K. Butiugin, L. G. Liberov and N. D. Stepanova	299	6	1152
The Potassium Content of Salt Deposits in Tuva. I. N. Lepeshkov, N. N. Romasheva and V. K. Solov'ev	303	6	1156
Preparation of Some Primary Alcohols Via Organoaluminum Compounds. A. M. Sladkov V. A. Markevich, I. A. Iavich, L. K. Luneva and V. N. Chernov	307	6	1159
The Effect of Formamide on Isomeric Methylenedicyclohexanone and Tricyclohexanolone. M. N. Talichenko and V. I. Vysotskii	311	6	1162
Synthesis of Alkylindans. A. V. Topchiev, E. S. Pokrovskaia and T. G. Stepantseva	313	6	1164
Phase Changes in the Sodium Sulfate – Carbonate System. A. N. Khlapova	317	6	1167

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